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Inorganic Reactions  
and Methods

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Volume 11

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# Inorganic Reactions and Methods

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# Inorganic Reactions and Methods

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## Volume 11

**Formation of Bonds to C, Si,  
Ge, Sn, Pb (Part 3)**

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# How to Use this Book

## 1. Organization of Subject Matter.

### 1.1. Logic of Subdivision and Add-On Chapters.

This volume is part of a series that describes all of inorganic reaction chemistry. The contents are subdivided systematically and so are the contents of the entire series: Using the periodic system as a correlative device, it is shown how bonds between pairs of elements can be made. Treatment begins with hydrogen making a bond to itself in  $H_2$  and proceeds according to the periodic table with the bonds formed by hydrogen to the halogens, the groups headed by oxygen, nitrogen, carbon, boron, beryllium and lithium, to the transition and inner-transition metals and to the members of group zero. Next it is considered how the halogens form bonds among themselves and then to the elements of the main groups VI to I, the transition and inner-transition metals and the zero-group gases. The process repeats itself with descriptions of the members of each successive periodic group making bonds to all the remaining elements not yet treated until group zero is reached. At this point all actual as well as possible combinations have been covered.

The focus is on the primary formation of bonds, not on subsequent reactions of the products to form other bonds. These latter reactions are covered at the places where the formation of those bonds is described. Reactions in which atoms merely change their oxidation states are not included, nor are reactions in which the same pairs of elements come together again in the product (for example, in metatheses or redistributions). Physical and spectroscopic properties or structural details of the products are not covered by the reaction volumes which are concerned with synthetic utility based on yield, economy of ingredients, purity of product, specificity, etc. The preparation of short-lived transient species is not described.

While in principle the systematization described above could suffice to deal with all the relevant material, there are other topics that inorganic chemists customarily identify as being useful in organizing reaction information and that do not fit into the scheme. These topics are the subject of eight additional chapters constituting the last four books of the series. These chapters are systematic only within their own confines. Their inclusion is based on the best judgment of the Editorial Advisory Board as to what would be most useful currently as well as effective in guiding the future of inorganic reaction chemistry.

## **1.2. Use of Decimal Section Numbers**

The organization of the material is readily apparent through the use of numbers and headings. Chapters are broken down into divisions, sections and subsections, which have short descriptive headings and are numbered according to the following scheme:

- 1. Major Heading
  - 1.1. Chapter Heading
    - 1.1.1. Division Heading
      - 1.1.1.1. Section Heading
        - 1.1.1.1.1. Subsection Heading

Further subdivision of a five-digit "slice" utilizes lower-case Roman numerals in parentheses: (i), (ii), (iii), etc. It is often found that as a consequence of the organization, cognate material is located in different chapters but in similarly numbered pieces, i.e., in parallel sections. Section numbers, rather than page numbers, are the key by which the material is accessed through the various indexes.

## **1.3. Building of Headings**

### **1.3.1. Headings Forming Part of a Sentence**

Most headings are sentence-fragment phrases which constitute sentences when combined. Usually a period signifies the end of a combined sentence. In order to reconstitute the context in which a heading is to be read, superior-rank titles are printed as running heads on each page. When the sentences are put together from their constituent parts, they describe the contents of the piece at hand. For an example, see 2.3 below.

### **1.3.2. Headings Forming Part of an Enumeration**

For some material it is not useful to construct title sentences as described above. In these cases hierarchical lists, in which the topics are enumerated, are more appropriate. To inform the reader fully about the nature of the material being described, the headings of connected sections that are superior in hierarchy always occur as running heads at the top of each page.

## **2. Access and Reference Tools**

### **2.1. Plan of the Entire Series (Front Endpaper)**

Printed on the inside of the front cover is a list, compiled from all 18 reaction volumes, of the major and chapter headings, that is, all headings that

are preceded by a one- or two-digit decimal section number. This list shows in which volumes the headings occur and highlights the contents of the volume that is at hand by means of a gray tint.

## 2.2. Contents of the Volume at Hand

All the headings, down to the title of the smallest decimal-numbered subsection, are listed in the detailed table of contents of each volume. For each heading the table of contents shows the decimal section number by which it is preceded and the number of the page on which it is found. Beside the decimal section numbers, successive indentations reveal the hierarchy of the sections and thereby facilitate the comprehension of the phrase (or of the enumerative sequence) to which the headings of hierarchically successive sections combine. To reconstitute the context in which the heading of a section must be read to become meaningful, relevant headings of sections superior in hierarchy are repeated at the top of every page of the table of contents. The repetitive occurrences of these headings is indicated by the fact that position and page numbers are omitted.

## 2.3. Running Heads

In order to indicate the hierarchical position of a section, the top of every page of text shows the headings of up to three connected sections that are superior in hierarchy. These running heads provide the context within which the title of the section under discussion becomes meaningful. As an example, the page of Volume 1 on which section 1.4.9.1.3 “in the Production of Methanol” starts, carries the running heads:

- 1.4. The Formation of Bonds between Hydrogen and O,S,Se,Te,Po
- 1.4.9. by Industrial Processes
- 1.4.9.1. Involving Oxygen Compounds

whereby the phrase “in the Production of Methanol” is put into its proper perspective.

## 2.4. List of Abbreviations

Preceding the indexes there is a list of those abbreviations that are frequently used in the text of the volume at hand or in companion volumes. This list varies somewhat in length from volume to volume; that is, it becomes more comprehensive as new volumes are published.

Abbreviations that are used incidentally or have no general applicability are not included in the list but are explained at the place of occurrence in the text.



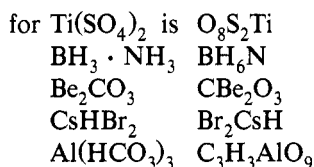
## 2.5. Author Index

The author index is compiled by computer from the lists of references. Thus it tells whose publications are cited and in that respect is comprehensive. It is not a list of authors, beyond those cited in the references, whose results are reported in the text. However, as the references cited are leading ones, consulting them, along with the use of appropriate works of the secondary literature, will rapidly lead to the complete literature related to any particular subject covered.

Each entry in the author index refers the user to the appropriate section number.

## 2.6. Compound Index

The compound index lists individual, fully specified compositions of matter that are mentioned in the text. It is an index of empirical formulas, ordered according to the following system: the elements within a given formula occur in alphabetical sequence except for C, or C and H if present, which always come first. Thus, the empirical formula



The formulas themselves are ordered alphanumerically without exception; that is, the formulas listed above follow each other in the sequence  $\text{BH}_6\text{N}$ ,  $\text{Br}_2\text{CsH}$ ,  $\text{CBe}_2\text{O}_3$ ,  $\text{C}_3\text{H}_3\text{AlO}_9$ ,  $\text{O}_8\text{S}_2\text{Ti}$ .

A compound index constructed by these principles tells whether a given compound is present. It cannot provide information about compound classes, for example, all aluminum derivatives or all compounds containing phosphorus.

In order to open this route of access as well, the compound index is augmented by successively permuted versions of all empirical formulas. Thus the number of appearances that an empirical formula makes in the compound index is equal to the number of elements it contains. As an example,  $\text{C}_3\text{H}_3\text{AlO}_9$ , mentioned above, will appear as such and, at the appropriate positions in the alphanumeric sequence, as  $\text{H}_3\text{AlO}_9 \cdot \text{C}_3$ ,  $\text{AlO}_9 \cdot \text{C}_3\text{H}_3$  and  $\text{O}_9 \cdot \text{C}_3\text{H}_3\text{Al}$ . The asterisk identifies a permuted formula and allows the original formula to be reconstructed by shifting to the front the elements that follow the asterisk.

Each nonpermuted formula is followed by linearized structural formulas that indicate how the elements are combined in groups. They reveal the connectivity of the compounds underlying each empirical formula and serve to

distinguish substances which are identical in composition but differ in the arrangement of elements (isomers). As an example, the empirical formula  $C_4H_{10}O$  might be followed by the linearized structural formulas  $(CH_3CH_2)_2O$ ,  $CH_3(CH_2)_2OCH_3$ ,  $(CH_3)_2CHOCH_3$ ,  $CH_3(CH_2)_3OH$ ,  $(CH_3)_2CHCH_2OH$  and  $CH_3CH_2(CH_3)CHOH$  to identify the various ethers and alcohols that have the element count  $C_4H_{10}O$ .

Each linearized structural formula is followed in a third column by keywords describing the context in which it is discussed and by the number(s) of the section(s) in which it occurs.

## 2.7. Subject Index

The subject index provides access to the text by way of methods, techniques, reaction types, apparatus, effects and other phenomena. Also, it lists compound classes such as organotin compounds or rare-earth hydrides which cannot be expressed by the empirical formulas of the compound index.

For multiple entries, additional keywords indicate contexts and thereby avoid the retrieval of information that is irrelevant to the user's need.

Again, section numbers are used to direct the reader to those positions in the book where substantial information is to be found.

## 2.8. Periodic Table (Back Endpaper)

Reference to periodic groups avoids cumbersome enumerations. Section headings in the series employ the nomenclature.

Unfortunately, however, there is at the present time no general agreement on group designations. In fact, the scheme that is most widely used (combining a group number with the letters A and B) is accompanied by two mutually contradictory interpretations. Thus, titanium may be a group IVA or group IVB element depending on the school to which one adheres or the part of the world in which one resides.

In order to clarify the situation for the purposes of the series, a suitable labeled periodic table is printed on the inside back cover of each volume. All references to periodic group designations in the series refer to this scheme.

## Preface to the Series

**Inorganic Reactions and Methods** constitutes a closed-end series of books designed to present the state of the art of synthetic inorganic chemistry in an unprecedented manner. So far, access to knowledge in inorganic chemistry has been provided almost exclusively using the elements or classes of compounds as starting points. In the first 18 volumes of **Inorganic Reactions and Methods**, it is bond formation and type of reaction that form the basis of classification.

This new route of access has required new approaches. Rather than sewing together a collection of review articles, a framework has had to be designed that reflects the creative potential of the science and is hoped to stimulate its further development by identifying areas of research that are most likely to be fruitful.

The reaction volumes describe methods by which bonds between the elements can be formed. The work opens with hydrogen making a bond to itself in  $H_2$  and proceeds through the formation of bonds between hydrogen and the halogens, the groups headed by oxygen, nitrogen, carbon, boron, beryllium and lithium to the formation of bonds between hydrogen and the transition and inner-transition metals and elements of group zero. This pattern is repeated across the periodic system until all possible combinations of the elements have been treated. This plan allows most reaction topics to be included in the sequence where appropriate. Reaction types that do not arise from the systematics of the plan are brought together in the concluding chapters on oxidative addition and reductive elimination, insertions and their reverse, electron transfer and electrochemistry, photochemical and other energized reactions, oligomerization and polymerization, inorganic and bioinorganic catalysis and the formation of intercalation compounds and ceramics.

The project has engaged a large number of the most able inorganic chemists as Editorial Advisors creating overall policy, as Editorial Consultants designing detailed plans for the subsections of the work, and as authors whose expertise has been crucial for the quality of the treatment. The conception of the series and the details of its technical realization were the subject of careful planning for several years. The distinguished chemists who form the Editorial Advisory Board have devoted themselves to this exercise, reflecting the great importance of the project.

It was a consequence of the systematics of the overall plan that publication of a volume had to await delivery of its very last contribution. Thus was the defect side of the genius of the system revealed, as the excruciating process of extracting the rate-limiting manuscripts began. Intense editorial effort was

required in order to bring forth the work in a timely way. The production process had to be designed so that the insertion of new material was possible up to the very last stage, enabling authors to update their pieces with the latest developments. The publisher supported the cost of a computerized bibliographic search of the literature and a second one for updating.

Each contribution has been subjected to an intensive process of scientific and linguistic editing in order to homogenize the numerous individual pieces, as well as to provide the highest practicable density of information. This had several important consequences. First, virtually all semblances of the authors' individual styles have been excised. Second, it was learned during the editorial process that greater economy of language could be achieved by dropping conventionally employed modifiers (such as *very*) and eliminating italics used for emphasis, quotation marks around nonquoted words, or parentheses around phrases, the result being a gain in clarity and readability. Because the series focuses on the chemistry rather than the chemical literature, the need to tell who has reported what, how and when can be considered of secondary importance. This has made it possible to bring all sentences describing experiments into the present tense. Information on who published what is still to be found in the reference lists. A further consequence is that authors have been burdened neither with identifying leading practitioners, nor with attributing priority for discovery, a job that taxes even the talents of professional historians of science. The authors' task then devolved to one of describing inorganic chemical reactions, with emphasis on synthetic utility, yield, economy, availability of starting materials, purity of product, specificity, side reactions, etc.

The elimination of the names of people from the text is by far the most controversial feature. Chemistry is plagued by the use of nondescriptive names in place of more expository terms. We have everything from Abegg's rule, Adkin's catalyst, Admiralty brass, Alfven number, the Amadori rearrangement and Adursov oxidation to the Zdanovskii law, Zeeman effect, Zincke cleavage and Zinin reduction. Even well-practiced chemists cannot define these terms precisely except for their own areas of specialty, and no single source exists to serve as a guide. Despite these arguments, the attempt to replace names of people by more descriptive phrases was met in many cases by a warmly negative reaction by our colleague authors, notwithstanding the obvious improvements wrought in terms of lucidity, freedom from obscurity and obfuscation and, especially, ease of access to information by the outsider or student.

Further steps toward universality are taken by the replacement of element and compound names wherever possible by symbols and formulas, and by adding to data in older units their recalculated SI equivalents. The usefulness of the reference sections has been increased by giving journal-title abbreviations according to the *Chemical Abstracts Service Source Index*, by listing in each reference all of its authors and by accompanying references to patents and journals that may be difficult to access by their *Chemical Abstracts* cita-

tions. Mathematical signs and common abbreviations are employed to help condense prose and a glossary of the latter is provided in each volume. Dangerous or potentially dangerous procedures are highlighted in safety notes printed in boldface type.

The organization of the material should become readily apparent from an examination of the headings listed in the table of contents. Combining the words constituting the headings, starting with the major heading (one digit) and continuing through the major chapter heading (two digits), division heading (three digits), section heading (four digits) to the subsection heading (five digits), reveals at once the subject of a "slice" of the plan. Each slice is a self-contained unit. It includes its own list of references and provides definitions of unusual terms that may be used in it. The reader, therefore, through the table of contents alone, can in most instances quickly reach the desired material and derive the information wanted.

In addition there is for each volume an author index (derived from the lists of references) and a subject index that lists compound classes, methods, techniques, apparatus, effects and other phenomena. An index of empirical formulas is also provided. Here in each formula the element symbols are arranged in alphabetical order except that C, or C and H if present, always come first. Moreover, each empirical formula is permuted successively. Each permuted formula is placed in its alphabetical position and cross referenced to the original formula. Therefore, the number of appearances that an empirical formula makes in the index equals the number of its elements. By this procedure all compounds containing a given element come together in one place in the index. Each original empirical formula is followed by a linearized structural formula and keywords describing the context in which the compound is discussed. All indexes refer the user to subsection rather than page number.

Because the choice of designations of groups in the periodic table is currently in a state of flux, it was decided to conform to the practice of several leading inorganic texts. To avoid confusion an appropriately labeled periodic table is printed on the back endpaper.

From the nature of the work it is obvious that probably not more than two persons will ever read it entire: myself and the publisher's copy editor, Dr. Lindsay S. Ardwin. She, as well as Ms. Mary C. Stradner, Production Manager of VCH Publishers, are to be thanked for their unflagging devotion to the highest editorial standards. The original conception for this series was the brainchild of Dr. Hans F. Ebel, Director of the Editorial Department of VCH Verlagsgesellschaft in Weinheim, Federal Republic of Germany, who also played midwife at the birth of the plan of these reaction volumes with my former mentor, Professor Alan G. MacDiarmid of the University of Pennsylvania, and me in attendance, during the Anaheim, California, American Chemical Society Meeting in the Spring of 1978. Much of what has finally emerged is the product of the inventiveness and imagination of Professor Helmut Gr newald, President of VCH Verlagsgesellschaft. It is a pleasure to

acknowledge that I have learned much from him during the course of our association. Ms. Nancy L. Burnett is to be thanked for typing everything that had to do with the series from its inception to this time. Directing an operation of this magnitude without her help would have been unimaginable. My wife Rose stood by with good cheer while two rooms of our home filled up with 10,000 manuscript pages, their copies and attendant correspondence.

Finally, and most important, an enormous debt of gratitude toward all our authors is to be recorded. These experts were asked to prepare brief summaries of their knowledge, ordered in logical sequence by our plan. In addition, they often involved themselves in improving the original conception by recommending further refinements and elaborations. The plan of the work as it is being published can truly be said to be the product of the labors of the advisors and consultants on the editorial side as well as the many, many authors who were able to augment more general knowledge with their own detailed information and ideas. Because of the unusually strict requirements of the series, authors had not only to compose their pieces to fit within narrowly constrained limits of space, format and scope, but after delivery to a short deadline were expected to stand by while an intrusive editorial process homogenized their own prose styles out of existence and shrank the length of their expositions. These long-suffering colleagues had then to endure the wait for the very last manuscript scheduled for their volume to be delivered so that their work could be published, often after a further diligent search of the literature to insure that the latest discoveries were being cited and that claims for facts now proved false were eliminated. To these co-workers (270 for the reaction volumes alone), from whom so much was demanded but who continued to place their knowledge and talents unstintingly at the disposal of the project, we dedicate this series.

J. J. ZUCKERMAN  
Norman, Oklahoma  
July 4, 1985

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## **5. The Formation of Bonds to Elements of Group IVB (C, Si, Ge, Sn, Pb) (Part 3)**

## 5.5. Formation of Bonds between Elements of Groups IVB (C, Si, Ge, Sn, Pb) and IA (Li, Na, K, Rb, Cs, Fr)

### 5.5.1. Introduction

In this chapter are found the reactions used to prepare the alkali-metal derivatives of the main fourth-group elements. Because of their great usefulness and the often unique conditions employed in organolithium reagent synthesis, the formation of the bond between carbon and lithium is singled out for separate treatment. After discussing the preparations of the organolithium compounds from lithium metal and its alloys and from other organolithium derivatives, the formation of the organic derivatives of the other group-IA metals is considered. Chapter 5.5 concludes with a description of how silyl-, germyl-, stannyl- and plumbyl-derivatives of the alkali metals are synthesized.

(J. J. ZUCKERMAN, ED.)

### 5.5.2. Carbon–Lithium Bonds

#### 5.5.2.1. from the Elements.

The carbides<sup>1–16</sup> can be divided into three groups based on the presence of C, C=C or C≡C groups in the lattice. Some carbides have a combination of these. The acetylide group is found in group IA. An interstitial subgroup of carbides forms between the group-IA elements and graphite. These graphidides have metal atoms occupying ordered positions between the hexagonal layers. Depending on the periodicity of the metal layers, the graphidides have the compositions MC<sub>6</sub> (stage I), MC<sub>12</sub> (stage II), MC<sub>18</sub> (stage III), MC<sub>48</sub> (stage IV), etc.

Some carbides exist over a composition range owing to vacancies in the carbon sublattice. Preoccupation with stoichiometric compositions causes measured properties to be assigned to this composition when the material is deficient in carbon. Further, vacancies in the deficient material can occur, thereby causing subtle changes in crystal structure and properties. This is frequently overlooked.

Industrial application of the carbides is based on their hardness for use as cutting tools, abrasives, or wear-resistant coatings; on their resistance to chemical attack in a reducing environment; and on their stability at high T.

Pure Li carbide is formed by direct reaction between elemental carbon and the liquid metal or its vapor at >450°C. Impure carbide results when Li carbonate and carbon react at 600°–800°C<sup>17,18</sup>. Acetylene acting on a solution of Li in NH<sub>3</sub> will produce a compound, Li<sub>2</sub>C<sub>2</sub>—C<sub>2</sub>H<sub>2</sub>—2 NH<sub>3</sub>, which can be decomposed by a stream of H<sub>2</sub> or inert gas at RT to release the white, finely divided Li<sub>2</sub>C<sub>2</sub> powder. The solid carbide is stable up to at least 925°C<sup>19</sup>, although it will preferentially vaporize to Li<sub>l(g)</sub> at lower T.

The stoichiometry of the intercalation compounds with graphite depends on the occupancy of the available positions in the graphite structure by Li atoms. The fully

saturated compound, stage I, has an ideal stoichiometry of  $\text{LiC}_6$  with the alternating layers containing Li atoms in an ordered array. This material can be prepared by subjecting a mixture of carbon in various forms and powdered Li metal to 10–20 kbar ( $1\text{--}2 \times 10^9$  Pa) at RT followed by annealing at  $200^\circ\text{C}$ . Alternatively, crystalline graphite can be heated in liquid or gaseous Li metal below  $500^\circ\text{C}$ <sup>20</sup>. Good yields are obtained when pyrolytic graphite is heated in liquid Li at  $350\text{--}400^\circ\text{C}$  for 8 h<sup>21,22</sup>. The stoichiometric material is brass-yellow. The blue, second-stage material, with a stoichiometry near  $\text{LiC}_{12}$ , consists of metal layers alternating with two graphite layers. Owing to Li vacancies, the actual material can have a composition lying within a range extending up to  $\text{LiC}_{18}$ , the third-stage composition<sup>21,22</sup>. The second-stage material is prepared by heating pyrolytic graphite in Na metal containing 3.8 wt % Li held at  $400^\circ\text{C}$  in a stainless-steel crucible for up to 8 h<sup>21–23</sup>. Higher stages, up to stage IV, are prepared by the direct reaction between powdered Li metal and carbon as pressed billets at  $200^\circ\text{C}$ <sup>20</sup>.

(E. K. STORMS)

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### 5.5.2.2. from Lithium and Its Alloys

#### 5.5.2.2.1. with Organic Halides.

**Organolithium solutions are pyrophoric and should be handled with care.**

Organolithiums may be prepared from the reaction of Li metal with organic halides with concomitant formation of Li halide<sup>1</sup>:



## 5.5. Formation of Bonds between Elements of Groups IVB and IA

3

## 5.5.2 Carbon–Lithium Bonds

saturated compound, stage I, has an ideal stoichiometry of  $\text{LiC}_6$  with the alternating layers containing Li atoms in an ordered array. This material can be prepared by subjecting a mixture of carbon in various forms and powdered Li metal to 10–20 kbar ( $1\text{--}2 \times 10^9$  Pa) at RT followed by annealing at 200°C. Alternatively, crystalline graphite can be heated in liquid or gaseous Li metal below 500°C<sup>20</sup>. Good yields are obtained when pyrolytic graphite is heated in liquid Li at 350–400°C for 8 h<sup>21,22</sup>. The stoichiometric material is brass-yellow. The blue, second-stage material, with a stoichiometry near  $\text{LiC}_{12}$ , consists of metal layers alternating with two graphite layers. Owing to Li vacancies, the actual material can have a composition lying within a range extending up to  $\text{LiC}_{18}$ , the third-stage composition<sup>21,22</sup>. The second-stage material is prepared by heating pyrolytic graphite in Na metal containing 3.8 wt % Li held at 400°C in a stainless-steel crucible for up to 8 h<sup>21–23</sup>. Higher stages, up to stage IV, are prepared by the direct reaction between powdered Li metal and carbon as pressed billets at 200°C<sup>20</sup>.

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## 5.5.2.2. from Lithium and Its Alloys

## 5.5.2.2.1. with Organic Halides.

**Organolithium solutions are pyrophoric and should be handled with care.**

Organolithiums may be prepared from the reaction of Li metal with organic halides with concomitant formation of Li halide<sup>1</sup>:



Chlorides are commonly employed for the formation of alkyllithiums, but bromides may be used also. Alkyl iodides, except methyl iodide, are not used because they couple with the organolithiums:



Aryllithiums are prepared from the bromides or iodides with Li metal; the less reactive aryl iodides do not lead to coupling products. Fluorides, with the exception of fluorobenzene and 1-fluoronaphthalene, are not used to prepare organolithiums.

The byproduct Li halide formed in reaction (a) is of no significance; however, complexes of organolithiums with Li halides have reactivities different from salt-free organolithiums<sup>2</sup>, and this can be important. Because LiCl is less soluble in ether than the bromide, low halide concentrations can be obtained in ether by using the organic chloride.

In the heterogeneous reaction (a), the rate is a function of the metal surface area. Less reactive organic halides require high-surface-area metal for the reaction to proceed. Lithium metal in the form of pieces cut from bars or wire often is employed. More metal surface area is obtained when the Li is first beaten into a sheet. Shot or dispersions prepared from molten metal provide high-surface-area metal. **Lithium dispersions are pyrophoric in humid atmospheres. Molten Li metal may attack glass**, and stainless steel reaction vessels are recommended for the preparation of dispersions. Etched glassware or chips of broken glass may be used to scour the metal and provide a fresh surface. The use of ultrasound with a standard laboratory ultrasonic bath can enhance rates<sup>3</sup>; this procedure also may serve to provide fresh metal surface. Lithium atoms<sup>4</sup> produced in a metal-atom reactor react with halogen or polyhalogen organic compounds.

Commercially supplied Li metal contains Na, which can be crucial for reaction (a). Lithium containing <0.005 % Na reacts poorly, whereas Li containing 0.8 % Na forms organolithiums in high yield<sup>5</sup>; the low-Na containing metal becomes coated during the attempted reactions. For laboratory preparations, Li-Na alloys containing 0.5–2.0 % Na are used, but higher Na-content alloys may be preferred in larger batch preparations<sup>4</sup>.

The choice of solvent for reaction (a) is important. Alkyllithiums (except CH<sub>3</sub>Li) react with ethers. Primary alkyllithiums may be prepared in ether if storage of the reagent is not necessary, or in the even more reactive tetrahydrofuran (THF) at low T (ca. –50°C) when the reagent is to be used promptly. For more reactive secondary and tertiary alkyllithiums, hydrocarbon solvents are used. The less reactive methyl-, aryl- and vinylolithiums are prepared in ethers.

Because organolithium reagents react with H<sub>2</sub>O, CO<sub>2</sub> and O<sub>2</sub>, an atmosphere of N<sub>2</sub> or Ar is employed for preparations and handling. Lithium metal can react with N<sub>2</sub>; therefore, at the high T required to melt Li metal (mp 182°C) for the preparation of shot or dispersion, inert gas atmospheres, such as Ar or He, are necessary.

Tertiary alkyllithiums are difficult to prepare by reaction (a), but optimum conditions for the preparation of t-butyllithium and other tertiary alkyllithiums are available<sup>6–8</sup> (see below).

(i) Methylolithium. Stable solutions of methylolithium in ether can be prepared from CH<sub>3</sub>Cl<sup>9</sup>, CH<sub>3</sub>Br<sup>10</sup> or CH<sub>3</sub>I<sup>11</sup> in 80–98 % yield. The reaction of CH<sub>3</sub>Cl with Li wire in THF at –10°C gives CH<sub>3</sub>Li in 77 % yield<sup>12</sup>, but the attempted formation of CH<sub>3</sub>Li in THF from CH<sub>3</sub>I fails<sup>12</sup>. Low-salt CH<sub>3</sub>Li (containing 5 % LiCl) can be prepared<sup>13</sup>.

Methylolithium is not soluble in hydrocarbons, nor can it be prepared by reaction (a) in hydrocarbons.

(ii) Primary Alkylolithiums. These are prepared in hydrocarbons in high yield by reacting the appropriate chloride or bromide with pieces of Li metal. Because of the possible reaction with ethers, the preparation of primary alkylolithiums in ethers is best conducted at ca.  $-10^{\circ}\text{C}$ , and preparations in THF usually are performed at lower T. Table 1 lists primary alkylolithiums prepared from alkyl chlorides and bromides. Moderate to high yields of the alkylolithiums in hydrocarbons or ether may be obtained.

The examples in the table show the available reagents, the conditions employed and the limits of utility of the reactions. The yields are the highest available and are determined by double titration of the organolithiums or by derivatization to give products that implicate stable organolithiums. Excluded are reagents not characterized or wherein the yields are inferred only by the ultimate yield of reduced products obtained after hydrolysis of the reaction mixture. Similarly excluded are cases in which in situ trapping agents are used to determine yields.

(iii) Secondary Alkylolithiums. These are more difficult to prepare via reaction (a) than are their primary counterparts. Yields are higher with chlorides because the bromide precursors react more readily in secondary reactions with the organolithiums. Because of the increased reactivity of secondary alkylolithiums, hydrocarbons are used in their preparation instead of ethers.

Cyclopropylolithiums are exceptions. These species are stabler than other secondary alkylolithium reagents and are prepared in ether from cyclopropyl bromides.

The stereochemical outcome of formation of secondary alkylolithiums from the corresponding halides suggests a complicated or mixed reaction mechanism. Cyclopropylolithiums form from cyclopropyl bromides with Li metal with predominant but low retention of stereochemistry<sup>29</sup>. Once formed, the cyclopropylolithiums maintain stereochemical integrity, and high stereoselectivity is possible when other methods of preparation, such as metal–halogen exchange, are used (see §5.5.2.3.3). Larger ring secondary alkylolithiums, such as menthylolithium (**C** in Fig. 1), are formed in the reaction of the chlorides with Li with complete equilibration at the carbon bonded to the metal<sup>30</sup>. Menthylolithium, is formed e.g., from both menthyl chloride and its C-1 epimer, isomenthyl chloride.

Table 2 lists secondary alkylolithium reagents, including the reagents shown in Fig. 1.

(iv) Tertiary Alkylolithiums. These reagents require care in preparation, and preparations are difficult to reproduce. Conditions may not be applicable for closely related species; e.g., controlled conditions for  $(\text{CH}_3)_3\text{CCl}$  reproducibly give 70–80% yield of product, but these conditions cannot be used<sup>6</sup> for  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Li}$ .

Tertiary alkylolithiums are prepared in hydrocarbons from the appropriate alkyl chlorides with Li dispersions. Once the reaction is initiated, secondary reactions between the reagent and its precursor halide may cause low yields. Slow rates of addition of the alkyl chloride minimize these secondary reactions<sup>7,8</sup>. Polycyclic and bridgehead reagents are less susceptible to such bimolecular reactions with their precursor chlorides.

As with secondary cyclopropylolithiums, the formation of a tertiary cyclopropylolithium is accompanied by partial racemization at the carbon–metal center<sup>40</sup>.

The preparation of  $(\text{CH}_3)_3\text{CClLi}$  from  $(\text{CH}_3)_3\text{CCl}$  in  $\leq 90\%$  yield<sup>6–8</sup> and the preparations of the tertiary alkylolithiums in Fig. 2 are available.

TABLE 1. PRIMARY ALKYL LITHIUMS PREPARED FROM LI METAL WITH ORGANIC HALIDES

RLi	Halide	Solvent (conditions) <sup>a</sup>	Yield (%)	Refs.
CH <sub>3</sub> CH <sub>2</sub> Li	Cl	Ether (–10°C)	88	14
	Br	Pentane	95	15
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Li	Cl	Pentane	80–95	14,15
	Cl	Ether (–10°C)	82	14
	Br	Petroleum ether	60	16
	Br	Ether (–10°C)	78	17
	Br	Ether <sup>b</sup>	90	3
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Li	Cl	Pentane	95	15
	Cl	Heptane (0.8% Na)	80	18
	Cl	Benzene (0.8% Na)	80	18
	Cl	Ether (–10°C)	89	14
	Cl	THF (–25°C)	74	12
	Br	Petroleum ether	70	16
	Br	Ether (–10°C)	90	17
	Br	THF (–60°C)	56	12
CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> Li	Cl	Pentane	85	19
	Cl	Ether (–10°C)	76	14
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> Li	Cl	Pentane	95	15
	Br	Ether (–10°C)	77	17
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> Li	Cl	Petroleum ether	60	20
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> Li	Cl	Pentane	63	14
	Cl	Ether (–10 °C)	76	14
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> Li	Br	Ether (–10°C)	77	17
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>2</sub> Li	Cl	Petroleum ether	86	21
	Cl	Ether	100	21
	Br	Ether	65	21
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH <sub>2</sub> Li	Br	Ether	64	21
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>2</sub> Li	Cl	Petroleum ether	63	21
	Cl	Ether	100	21
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>2</sub> Li	Br	Ether	56	21
n-C <sub>n</sub> H <sub>2n+1</sub> Li <sup>c</sup>	Br	Ether	<sup>d</sup>	22
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CHCH <sub>2</sub> Li	Br	Ether	<sup>d</sup>	22
CH <sub>3</sub> OCH <sub>2</sub> Li	Cl	(CH <sub>3</sub> O) <sub>2</sub> CH <sub>2</sub>	80	23
(CH <sub>3</sub> CH <sub>2</sub> O) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> Li	Br	Ether	60	24
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> Li	Cl	Pentane	66	25
CH <sub>3</sub> C≡CC(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>2</sub> Li	Cl	THF (–75 °C)	83	26
(CH <sub>3</sub> ) <sub>3</sub> CC≡CC(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>2</sub> Li	Cl	THF (–75°C)	89	26
C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Li	Cl	THF (–65°C)	71	27
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> Li	Cl	Ether (0°C)	59	28

<sup>a</sup> Special reaction conditions are given. If conditions are not specified, the reactions are run at RT or in refluxing solvent.

<sup>b</sup> Ultrasonic irradiation is employed.

<sup>c</sup> The alkylolithiums with n = 8–11, 14, 16, and 18 are prepared in unspecified yield.

<sup>d</sup> Not available.



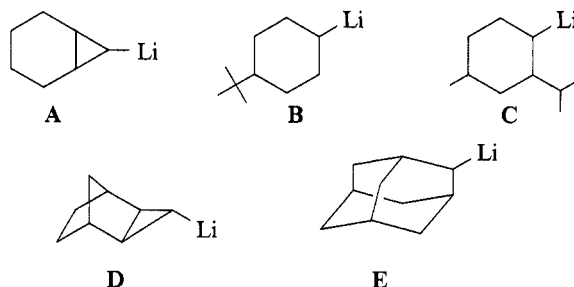


Figure 1. Some secondary alkyllithiums (see Table 2).

TABLE 2. SECONDARY ALKYL LITHIUMS PREPARED FROM LI METAL WITH ORGANIC HALIDES

RLi	Halide	Solvent (T) <sup>a</sup>	Yield (%)	Ref.
(CH <sub>3</sub> ) <sub>2</sub> CHLi	Cl	Petroleum ether	88	11
	Cl	Pentane	75	19
	Cl	Ether (–50°C)	<sup>b</sup>	31
	Br	Pentane	15	19
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )Li	Cl	Pentane	95	15
	Cl	Ether	27	9
$\overline{\text{CH}_2\text{CH}_2\text{CHLi}}$	Cl	Pentane	70	32
	Cl	Ether (0°C)	66	33
	Br	Ether	55	34
$\overline{\text{R}_2\text{CCR}_2\text{CHLi}}$ <sup>c</sup>	Br	Ether	87–100	34
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CHLi}}$	Cl	Pentane	50	14
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHLi}}$	Cl	Pentane	51	14
$\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHLi}}$	Cl	Petroleum ether	25	35
	Cl	Pentane	28	36
	Cl	Ether	24	37
	Br	Ether	98	34
C <sub>8</sub> H <sub>11</sub> Li <sup>d</sup>	Cl	Pentane	35	38
C <sub>10</sub> H <sub>19</sub> Li <sup>e</sup>	Cl	Pentane	60	30
C <sub>10</sub> H <sub>19</sub> Li <sup>f</sup>	Cl	Ether (0°C)	75	39
C <sub>8</sub> H <sub>11</sub> Li <sup>g</sup>	Cl	Pentane	85	8
C <sub>10</sub> H <sub>15</sub> Li <sup>h</sup>				

<sup>a</sup> Special conditions are given; if none is specified the reactions are run at RT or in refluxing solvent.

<sup>b</sup> Not available.

<sup>c</sup> The substituted cyclopropyllithiums prepared are 2-ethyl-, 2,2-dimethyl-, cis-2,3-dimethyl-, trans-2,3-dimethyl-, 2,2,3-trimethyl- and 2,2,3,3-tetramethylcyclopropyllithium.

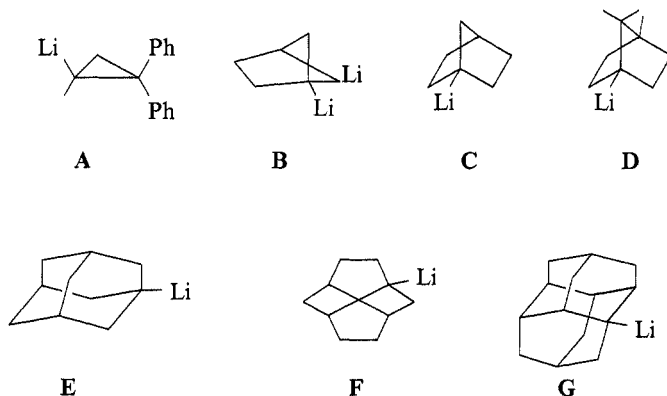
<sup>d</sup> 7-Lithiobicyclo[4.1.0]heptane (A in Fig. 1).

<sup>e</sup> 4-t-Butylcyclohexyllithium (B in Fig. 1).

<sup>f</sup> Menthyllithium (C in Fig. 1).

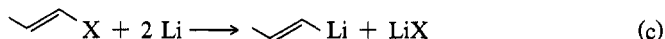
<sup>g</sup> 3-Lithiotricyclo[3.2.1.0<sup>2,4</sup>]octane (D in Fig. 1).

<sup>h</sup> 2-Adamantyllithium (E in Fig. 1).



**Figure 2.** Tertiary alkyllithiums: (A) 1-methyl-2,2-diphenylcyclopropyllithium, 74 %<sup>40</sup>; (B) 1-lithiobicyclo[2.1.1]hexane, 83 %<sup>41</sup>; (C) 1-lithiobicyclo[2.2.1]heptane, > 51 %<sup>42</sup>; (D) 1-lithio-4,7,7-trimethylbicyclo[2.2.1]heptane, 72 %<sup>43</sup>; (E) 1-lithioadamantane, > 80 %<sup>43</sup>; (F) 1-lithiotwistane, 90 %<sup>8</sup>; (G) 1-lithiobiadamantane, 76 %<sup>8</sup>.

(v) **Vinylolithiums.** These compounds are prepared from the reaction of the appropriate vinyl chloride or bromide with Li metal. The reaction is stereospecific and highly stereoselective, giving rise to products with retention of configuration at the  $sp^2$ -hybridized carbon:



However, some isomerization frequently is observed. Although most vinylolithiums are configurationally stable, the  $\alpha$ -aryl vinylolithiums (prepared from metal-halogen exchange, see §5.5.2.3.3) equilibrate<sup>44</sup> in the presence of donor solvents, such as THF. Vinylolithiums are stable in ether, in which most preparations are performed (see Table 3).

(vi) **Aryllithiums.** These reagents are available from the reaction of aryl halides with Li metal in ethers. Hydrocarbons are not employed; phenyllithium is not soluble in hydrocarbons. Aryl bromides give high yields of aryllithiums, but other halides may be used. Substituted aryls work, and naphthyllithiums are produced (see Table 4). For larger polycyclic aromatic compounds, metal reduction of the aromatic moiety occurs; e.g., on extended treatment with Li metal, 9-bromoanthracene is reduced to the dilithium dianion. Even naphthyl chlorides can be reduced beyond the first formed aryllithium reagents (see §5.5.2.2.2). Therefore, the synthesis of polycyclic aromatic Li reagents requires alternative methods, such as metal-halogen exchange (see §5.5.2.3.3).

(vii) **Benzyl- and Allyllithiums.** These reagents cannot be prepared from the reaction of the corresponding halides with Li metal because coupling reactions between the Li reagents and these reactive organic halides, Eq. (b), are too fast. Attempted preparation of benzylolithium from benzyl chloride and Li affords only 1.4 % yield of phenylacetic acid after carboxylation<sup>66</sup>. These reagents are available from the corresponding Hg compounds (see §5.5.2.2.2), by Li cleavage of ethers (see §5.5.2.2.5), or by deprotonations (see §5.5.2.3.2).

Nevertheless, some hindered benzylic halides react with Li to give the corresponding organolithiums. Triphenylmethylolithium can be prepared in several solvents from the

TABLE 3. VINYL LITHIUMS PREPARED FROM VINYL HALIDES WITH LI METAL

RLi	Halide	Solvent (T) <sup>a</sup>	Yield (%)	Ref.
H <sub>2</sub> C=CHLi	Cl	THF (10°C)	65	45
cis-CH <sub>3</sub> CH=CHLi	Br	Ether (–28°C)	95 <sup>b</sup>	46
trans-CH <sub>3</sub> CH=CHLi	Cl	Ether (0°C)	98 <sup>b</sup>	46
	Br	Ether	67 <sup>c</sup>	47
cis-CH <sub>3</sub> CH=C(CH <sub>3</sub> )Li	Br	Ether (–28°C)	High <sup>d</sup>	46
trans-CH <sub>3</sub> CH=C(CH <sub>3</sub> )Li	Br	Ether (–28°C)	High <sup>d</sup>	46
(CH <sub>3</sub> ) <sub>2</sub> C=CHLi	Br	Ether	21	48
(CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> )Li	Br	Ether	17	49
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=CLi	Cl	Ether	14	50
	Cl	THF (–10°C)	85	51
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CLi	Cl	Ether	60	52
	Cl	Petroleum ether	0 <sup>e</sup>	52
	Cl	THF	0 <sup>e</sup>	51
(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH=CLi	Cl	Ether	63	53
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CLi	Cl	Ether	24	54
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=CLi	Br	Ether	30	55

<sup>a</sup> Unless stated, the reactions are run at RT or in refluxing solvent.

<sup>b</sup> The compounds are contaminated with 3% of the opposite diastereomer.

<sup>c</sup> The compound is contaminated with 10% of the cis isomer.

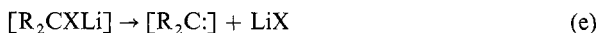
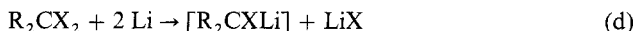
<sup>d</sup> The compounds are contaminated with 7% of the opposite diastereomer.

<sup>e</sup> The reaction fails to give the organolithium.

corresponding chloride in ≤ 70 % yield<sup>67</sup>, and 1-triptycyl lithium in ether can be prepared from the chloride in 93 % yield<sup>8</sup>. Diphenylmethyl lithium is formed from the chloride with Li metal, although this reaction may proceed by initial formation of 1,1,2,2-tetraphenylethane, which is then cleaved by the metal (see §5.5.2.2.5)<sup>68</sup>.

(viii) Dilithiums. Compounds containing two C–Li bonds may be prepared by reaction of some dihalides with Li metal (see Table 5). If the halogen-substituted carbons in an alkyl dihalide are separated by two or more carbons, dilithium reagent formation is possible. In these compounds formation of each C–Li bond proceeds independently of the other functional group.

A geminal dihalide could undergo rapid α-elimination after formation of one C–Li bond:



However, α-halolithiums can be prepared in high yield at low T by alternate procedures, such as deprotonation (see §5.5.2.3.2). Vicinal dihalides eliminate to give alkenes after forming one C–Li bond, as illustrated for 1,2-dibromoethane:

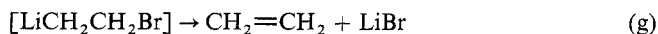


TABLE 4. ARYL LITHIUMS PREPARED FROM ARYL HALIDES WITH LI METAL

RLi	Halide	Solvent (T) <sup>a</sup>	Yield (%)	Ref.
C <sub>6</sub> H <sub>5</sub> Li	F	THF (–10°C)	50	56
	Cl	Ether	49	37
	Br	Ether	98	37
	Br	THF (–60°C)	98	12
	I	Ether	83	37
p-(n-C <sub>12</sub> H <sub>25</sub> )C <sub>6</sub> H <sub>4</sub> Li	Br	Ether	94–99	37
o-, m- or p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Li	Br	Ether	75	57
m-[(CH <sub>3</sub> ) <sub>3</sub> C]C <sub>6</sub> H <sub>4</sub> Li	Br	Ether	15	58
o-CH <sub>3</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Li	I	Ether	<sup>b</sup>	59
2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> Li	Br	Ether	82	60
2,6-(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Li	Br	Ether	72	61
o- or p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> Li	Br	Ether	88	37
o- or p-CH <sub>3</sub> CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> Li	Br	Ether	83–93	37
p-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Li	Br	Ether	96	37
p-(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Li	Br	Ether	58	62
o-, m- or p-C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> Li	Br	Ether	72–87	63
p-(CH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> GeC <sub>6</sub> H <sub>4</sub> Li	Br	Ether	90	64
1-C <sub>10</sub> H <sub>7</sub> Li <sup>c</sup>	F	THF (2°C)	23	37
	Br	Ether	96	37
2-C <sub>10</sub> H <sub>7</sub> Li <sup>d</sup>	Br	Ether	96	65

<sup>a</sup> Unless otherwise stated the reactions are run at RT or in refluxing solvent.<sup>b</sup> Not available.<sup>c</sup> 1-Naphthyllithium.<sup>d</sup> 2-Naphthyllithium.

Similarly, 1,2-dihaloarenes give benzyne intermediates, although 1,2-dilithiobenzene may be prepared from a mercurial (see §5.5.2.2.2).

1,3-Dilithioalkanes are not prepared from 1,3-dihaloalkanes. The products from Cl(CH<sub>2</sub>)<sub>3</sub>Cl and other  $\alpha,\omega$ -dichlorides with Li metal in heptane are not characterized<sup>69</sup>.

Table 5 lists the dilithiums. Dihalogens with active metals in the presence of in situ trapping agents lead to disubstituted products<sup>70</sup>, but in many cases there is no evidence that dilithiums are formed.

TABLE 5. DILITHIUMS PREPARED FROM DIHALIDES WITH LI METAL

Dilithium reagent	Halide	Solvent	T (°C)	Yield (%)	Refs.
Li <sub>2</sub> CH <sub>2</sub>	Br	Ether	–25	6	71,72
Li(CH <sub>2</sub> ) <sub>4</sub> Li	Br	Ether	–10	63	71,72
Li(CH <sub>2</sub> ) <sub>5</sub> Li	Br	Ether	–10	68	71,72
Li(CH <sub>2</sub> ) <sub>6</sub> Li	Br	Ether	–10	42	71,72
Li(CH <sub>2</sub> ) <sub>10</sub> Li	Br	Ether	–10	71	71,72
C <sub>6</sub> H <sub>10</sub> Li <sub>2</sub> <sup>a</sup>	Cl	Cyclohexane	25	25	73
1,4-Li <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Br	THF	–40	92	74
2,2'-Li <sub>2</sub> C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub>	Br	Ether	25	91	75
	I	Ether	25	93	76

<sup>a</sup> 1,4-Dilithiobicyclo[2.2.1]heptane.

(ix) Reactions of Li Atoms with Organic Halides. Lithium atoms formed in a metal-atom reactor react with organic substrates. Limited amounts with organic halides in an inert matrix give organic radicals and Li-halide salts<sup>77</sup>. Excess Li atoms at high T with short-chain organic halides and polyhalides give perlithiated derivatives, often with C–C bond scission. For example, treatment of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  with xs Li vapor at 300–1000°C leads to  $\text{C}_3\text{Li}_8$  in 20% yield<sup>78</sup>, among other products, and treatment of  $\text{CCl}_4$  under similar conditions gives  $\text{CLi}_4$  in 18% yield<sup>79</sup>. Treatment of  $\text{Cl}(\text{CH}_2)_5\text{Cl}$  and  $\text{Cl}(\text{CH}_2)_6\text{Cl}$  with Li vapor under milder conditions gives the corresponding  $\alpha,\omega$ -dilithiums, each in 31% yield, although only perlithiated products are obtained<sup>80</sup> from  $\text{XCH}_2\text{CH}_2\text{CH}_2\text{X}$  (X = Cl, Br). Lithiated carbocations such as  $[\text{CLi}_5]^+$  also form from  $\text{CCl}_4$  and Li vapor<sup>81</sup>.

(x) Organolithiums from Alkyl Halides with Li Aromatic Radical Anions. A potentially useful approach to the synthesis of organolithiums involves the application of

TABLE 6. ORGANOLITHIUMS PREPARED FROM  
 ORGANIC HALIDES WITH LI AROMATIC RADICAL ANIONS IN THF

RLi	Halide	$[\text{Ar}]^-\text{Li}^+$ <sup>a</sup>	T (°C)	Yield (%)	Ref.
$\text{CH}_3(\text{CH}_2)_1\text{CH}_2\text{Li}$	Cl	Phen	–100	45	84
$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Li}$	Cl	Naph	–78	45	85
	Cl	DTBB	–78	94	85
	Br	Naph	–78	47	85
	Br	DTBB	–78	91	85
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{Li}$	Cl	DTBB	–100	30	86
$\text{CH}_2\text{CHOCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$	Cl	Naph	–70	64	87
$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{Li}$	Cl	Naph	–78	24	85
	Cl	DTBB	–78	87	85
	Br	Naph	–78	25	85
	Br	DTBB	–78	83	85
$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{Li})\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	Br	DTBB	–78	90	83
$\text{CH}_2(\text{CH}_2)_4\text{CHLi}$	Cl	Naph	–50	70	84
$\text{C}_{10}\text{H}_{19}\text{Li}^b$	Cl	DTBB	–78	88	85
$\text{C}_7\text{H}_{11}\text{Li}^c$	Cl	Naph	–78	65	85
	Cl	DTBB	–78	95	85
$\text{C}_8\text{H}_{11}\text{Li}^d$	Cl	DTBB	–78	89	85
$\text{C}_7\text{H}_{11}\text{Li}^e$	Cl	DTBB	–78	96	86
$\text{CH}_3(\text{CH}_2)_3\text{C}(\text{CH}_2\text{CH}_3)(\text{CH}_3)\text{Li}$	Cl	Naph	–78	74	85
	Cl	DTBB	–78	95	85
$(\text{CH}_3)_3\text{CCHCH}_2\text{CH}=\text{C}(\text{Li})\text{CH}_2\text{CH}_2$	Cl	DTBB	–20	76	85
$\text{C}_6\text{H}_5\text{Li}$	F	Naph	–50	91	84
	Cl	Naph	5	89	84
$(\text{C}_6\text{H}_5)_2\text{CHLi}$	Cl	Phen	–50	13	84
	Cl	Naph	25	71	89
$(\text{C}_6\text{H}_5)_3\text{CLi}$	Cl	Phen	25	70	84
	Cl	Naph	25	100	89

<sup>a</sup> Phen, Li phenanthrene; Naph, Li naphthalene. DTBB, Li 4,4'-di(t-butyl)biphenyl.

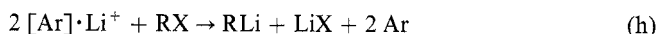
<sup>b</sup> 4-Butylcyclohexyllithium.

<sup>c</sup> 7-Lithiobicyclo[4.1.0]heptane.

<sup>d</sup> 3-Lithiotricyclo[3.2.1.0<sup>2,4</sup>]octane.

<sup>e</sup> 7-Lithionorborene.

an Li aromatic radical anion ( $[\text{Ar}] \cdot \text{Li}^+$ ) as a source of so-called soluble Li metal. Radical anions can react with organic halides to give organolithiums<sup>82</sup>:



analogous to Eq. (a). When a hindered aromatic compound is used, the electron-transfer processes of Eq. (h) are favored over alkylation, and high yields of organolithiums are achieved (see Table 6). The method is applicable to most organolithiums, from benzylic to tertiary. Organolithiums are produced in THF at low T where deprotonation of the solvent is minimized. Lithium naphthalene is less successful in reaction (h) than is the hindered Li 4,4'-di-tert-butylbiphenyl; the less hindered radical anion can couple with the halide more readily (see Table 6). The stereochemistry of Li 4,4'-di-t-butylbiphenyl reactions with secondary halides is known<sup>90</sup>; depending upon the substrate it reflects the relative stabilities of the intermediate radicals or the RLi products. Catalytic amounts of the aromatic species in the presence of Li metal can give comparable results, as is observed in the cleavages of alkylphenylsulfides by a similar method (see §5.5.2.2.5).

This method suffers from the presence of the aromatic species in the product mixture, leading to purification difficulties, but the high yield of many different organolithiums makes the method attractive. For example, conversion of 4-bromo-octa-1,7-diene to the corresponding alkylolithium with Li metal is not successful, but the secondary alkylolithium is obtained<sup>83</sup> in 90% yield from the bromide with Li 4,4'-di-tert-butylbiphenylide.

(M. E. NEWCOMB)

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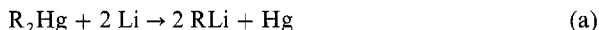
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#### 5.5.2.2.2. with Organomercurials.

**Organolithium solutions are pyrophoric and should be handled with caution. Dialkylmercury(II) compounds are toxic; furthermore, the lower members are volatile.**

Diorganomercury(II) compounds react with Li metal to give organolithiums and Hg, a reaction best referred to as a metal displacement but often called a transmetallation<sup>1</sup>:



Although the reaction is energetically favored in the forward direction, it is reversible, being driven toward formation of the organomercurials, in part, by the formation of Li amalgam, which removes Li from the reaction<sup>2</sup>. Therefore, the reaction is run in the presence of xs Li metal.

For a discussion of Li metal and the solvents and atmospheres appropriate for organolithiums, see the introduction to §5.5.2.2.1.

The preparation of organolithiums by reaction (a) is of limited synthetic utility because the organomercurials are prepared from other organometallic reagents, most often organomagnesium halides or organolithiums. In addition, reaction (a) is slow, although ultrasonic irradiation increases the rate.

However, reaction (a) can be useful. Organolithiums can be prepared free of salt and in high purity by appropriate choice of solvents, although contamination by organomercurials can be a problem. Salt-free organolithiums are more reactive than salt-complexed species<sup>4</sup>; e.g., salt-free  $\text{C}_6\text{H}_5\text{Li}$  prepared from the reaction of  $(\text{C}_6\text{H}_5)_2\text{Hg}$  with Li metal reacts with ether in 2–3 days<sup>5</sup>. In addition, organolithiums not available from the reaction of Li metal with organic halides such as  $\text{C}_6\text{H}_5\text{CH}_2\text{Li}$ , or ones that are prepared with difficulty from organic halides, can be prepared in high yield by reaction (a).

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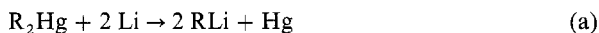
14      5.5. Formation of Bonds between Elements of Groups IVB and IA  
           5.5.2. Carbon–Lithium Bonds  
           5.5.2.2. from Lithium and Its Alloys

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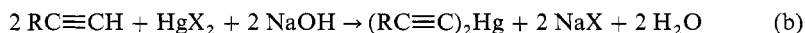
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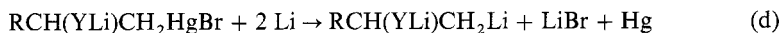
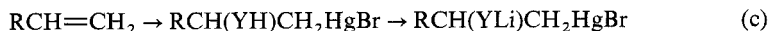
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Organomercurials prepared by oxy- or aminomercuration of alkenes are converted to Li reagents<sup>6</sup>:



where Y = O, NR.

Table 1 contains examples of organolithiums prepared by reaction (a). The preparation of  $\text{CH}_3\text{Li}$  by this reaction proceeds too slowly to be useful<sup>7</sup>. In addition to

TABLE 1. ORGANOLITHIUMS PREPARED FROM ORGANOMERCURIALS WITH LI METAL<sup>a</sup>

RLi	Solvent	T (°C)	Yield (%)	Refs.
$\text{CH}_3\text{CH}_2\text{Li}$	Benzene	20	60-70	9
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$	Benzene	65	<sup>b</sup>	7
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Li}$	<sup>c</sup>	<sup>b</sup>	<sup>b</sup>	10
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{Li}$	Cyclopentane	20	100	11
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{Li}^{\text{d}}$	<sup>e</sup>	20	<sup>b</sup>	12
$\text{C}_6\text{H}_5\text{CH}_2\text{Li}$	Ether	<sup>b</sup>	65	13
	THF, DME	-30	High	3
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\text{Li}$	Pentane	55-60	<sup>b</sup>	14
$(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_3)\text{CH}_2\text{Li}$	Ether	0	30	15
$\text{C}_6\text{H}_5\text{SCH}_2\text{Li}$	THF	<sup>b</sup>	<sup>b</sup>	16
$\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Li}$	2-Me-THF <sup>f</sup>	0	<sup>b</sup>	3
$\text{RCH}(\text{YLi})\text{CH}_2\text{Li}^{\text{g}}$	THF	-78	ca. 80	6
$\text{CH}_2\text{CH}_2\text{CHLi}$	Pentane	20	32	17
$\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{Si}(\text{CH}_3)_3^{\text{h}}$	THF, DME	0	<sup>b</sup>	3
$\text{CH}_2=\text{CHLi}$	Pentane	Reflux	70-80	18
$\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{CLi}$	Dioxane	<sup>b</sup>	58	19
$\text{CH}_3(\text{CH}_2)_{14}\text{C}\equiv\text{CLi}$	Dioxane	<sup>b</sup>	76	20
$3\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}\equiv\text{CLi}$	Dioxane	<sup>b</sup>	22	19
$\text{C}_6\text{H}_5\text{Li}$	Ether	20	<sup>b</sup>	5
$\text{p-CH}_3\text{C}_6\text{H}_4\text{Li}$	Ether	20	<sup>b</sup>	5
$2\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Li}$	Ether	20	98	21
$\text{o-C}_6\text{H}_4\text{Li}_2^{\text{i}}$	Ether	20	80-90	22
$2,2'\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Li}_2^{\text{j}}$	Ether	20	<sup>b</sup>	21
$2,2'\text{-o-LiC}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Li}^{\text{k}}$	Ether	20	64	23
$\text{CH}_3\text{CHLi}_2$	Ether	20	100	24

<sup>a</sup> Unless otherwise specified, RLi is prepared from the corresponding  $\text{R}_2\text{Hg}$ .

<sup>b</sup> Not available.

<sup>c</sup> Solvents used are pentane, ether and toluene.

<sup>d</sup> Prepared from  $[\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}_2]_2\text{Hg}$ . The first-formed organolithium rearranges.

<sup>e</sup> Solvents used are pentane, benzene and ether.

<sup>f</sup> 2-Me-THF = 2-methyltetrahydrofuran.

<sup>g</sup> Y = O, R =  $\text{C}_6\text{H}_5$ ; Y =  $\text{NC}_6\text{H}_5$ , R = H,  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ . The reagents are prepared from the corresponding hydroxy- or aminomercury(II) bromide by sequential treatment with  $\text{C}_6\text{H}_5\text{Li}$  and Li metal.

<sup>h</sup> Prepared from  $[\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2]_2\text{Hg}$ . The first-formed organolithium rearranges.

<sup>i</sup> Prepared from the cyclic hexamer  $(\text{o-C}_6\text{H}_4\text{Hg})_6$ .

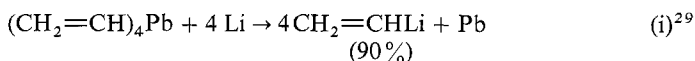
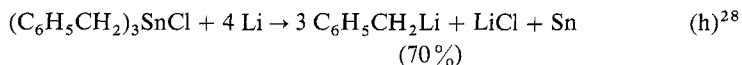
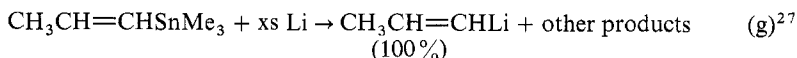
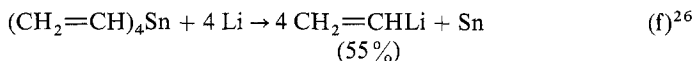
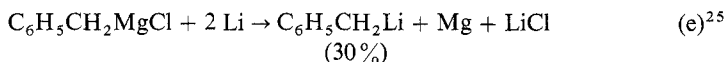
<sup>j</sup> Prepared from 2,2'-( $\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ )Hg.

<sup>k</sup> Prepared from the cyclic dimer  $(2,2'\text{-o-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_2$ .

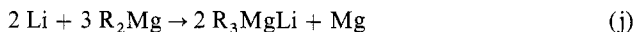
<sup>l</sup> From  $\text{CH}_3\text{CH}(\text{HgCl})_2$ .

the reactions in Table 1, the reaction of  $\text{Et}_2\text{Hg}$  with Li vapor at  $800^\circ\text{C}$  gives  $\text{C}_2\text{Li}_6$  in high yield<sup>8</sup>.

In reactions directly analogous to reaction (a), other organometallic reagents may undergo metal displacement by Li:



Lithium reacts with dialkylmagnesiums to give complexed organometallic reagents<sup>29</sup>:



(M. E. NEWCOMB)

1. General reviews of the preparations, properties and reactions of organolithiums are: B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1974; U. Schöllkopf, in *Methoden der Organischen Chemie*, Vol. XIII/1, E. Müller, ed., Georg Thieme Verlag, Stuttgart, 1970, p. 87.
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26. E. C. Juenge, D. Seyferth, *J. Org. Chem.*, **26**, 563 (1961).
27. D. Seyferth, R. Suzuki, L. G. Vaughan, *J. Am. Chem. Soc.*, **88**, 286 (1966).
28. D. Seyferth, R. Suzuki, C. J. Murphy, C. R. Sabat, *J. Organomet. Chem.*, **2**, 431 (1964).
29. D. B. Malpass, J. F. Eastham, *J. Org. Chem.*, **38**, 3718 (1973).

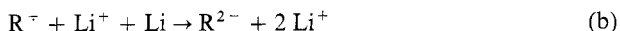
### 5.5.2.2.3. with Adducts of Conjugated Hydrocarbons in Donor Solvents.

**Organolithium solutions are pyrophoric and should be handled with care.**

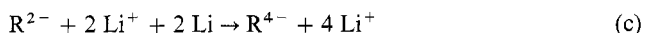
Organolithiums may be formed by the reduction of an organic compound with Li metal<sup>1,2</sup>. These reactions occur with aromatic species, conjugated olefins and carbonyl compounds containing low-energy antibonding orbitals. In the reductions, electrons are added into these orbitals in stages. A single reduction of a substrate gives a paramagnetic radical anion–cation pair:



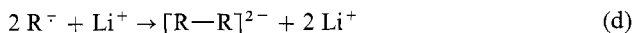
Further reduction of the radical anion gives a dianion, usually diamagnetic:



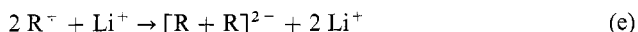
Even further reduction can occur, leading to tetraanions:



As an alternative to Eq. (b), radical anions couple to give dimeric dianions:

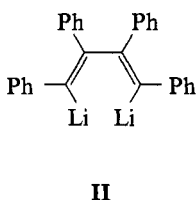
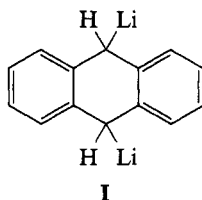


Further, the first-formed radical anions may be unstable to disproportionation:



Radical anions and dianions are strong bases, and in the presence of a protic source, these species can be protonated. The overall process, electron transfer from a metal followed by proton transfer, results in radicals that, after another cycle of electron transfer and proton transfer, produce reduced substrates. The transient radical anions, radicals and anions formed in these dissolving metal reductions are not considered in this section<sup>3</sup>. However, where the proton source is another substrate molecule, proton transfer gives an organolithium; formation of organolithiums by such a sequence is discussed in §5.5.2.2.4.

The reduction in Eq. (a) occurs with conjugated organic substrates. The radical anions formed often contain the added electron in a highly delocalized orbital, and these species cannot be represented by classical structures. Similarly, the dianions formed in Eq. (b) should be represented with delocalized structures. Nevertheless, classical structures that indicate the major resonance contributors are used; e.g., the dilithioanthracene dianion is represented as I:



5.5. Formation of Bonds between Elements of Groups IVB and IA 17  
 5.5.2. Carbon–Lithium Bonds  
 5.5.2.2. from Lithium and Its Alloys

25. K. Ziegler, F. Dersch, *Chem. Ber.*, **64**, 448 (1931).
26. E. C. Juenge, D. Seyferth, *J. Org. Chem.*, **26**, 563 (1961).
27. D. Seyferth, R. Suzuki, L. G. Vaughan, *J. Am. Chem. Soc.*, **88**, 286 (1966).
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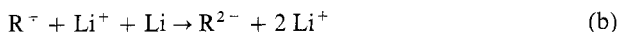
**5.5.2.2.3. with Adducts of Conjugated Hydrocarbons in Donor Solvents.**

**Organolithium solutions are pyrophoric and should be handled with care.**

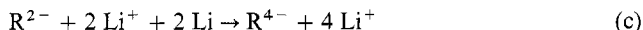
Organolithiums may be formed by the reduction of an organic compound with Li metal<sup>1,2</sup>. These reactions occur with aromatic species, conjugated olefins and carbonyl compounds containing low-energy antibonding orbitals. In the reductions, electrons are added into these orbitals in stages. A single reduction of a substrate gives a paramagnetic radical anion–cation pair:



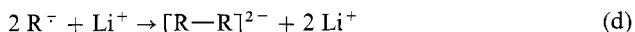
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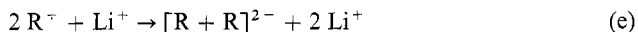
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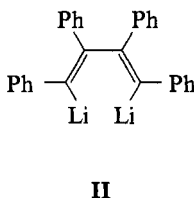
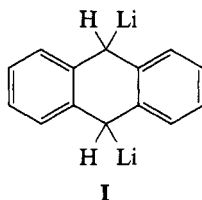


Further, the first-formed radical anions may be unstable to disproportionation:



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For the coupling reaction, Eq. (d), the dianion formed contains localized C–Li bonds (see II, the coupling product formed from reduction of  $C_6H_5C\equiv CC_6H_5$ ).

The solvent employed in the reduction can be critical in determining the course of the reaction. Donor solvents, e.g., ethers, often are used. The donor solvents stabilize the  $Li^+$  cation, making the reaction energetically feasible; e.g.,  $C_6H_5CH=CHC_6H_5$  with Li metal to give a dianion proceeds to at least 50% completion within a few hours in ether or dimethoxyethane (DME), but not in benzene even after extended reaction<sup>4</sup>. The popular ethereal solvents are DME and tetrahydrofuran (THF); often ether is not an adequate solvent. Hexamethylphosphoric triamide (HMPA) complexes Li strongly and may be used as a solvent. **Hexamethylphosphoric triamide causes tumors and should be handled in a hood with appropriate protective measures<sup>5</sup>.**

The choice of donor solvent can affect the course of reaction subtly. This is not seen in reactions of Li metal with halides or ethers; e.g., the value for the equilibrium constant for:

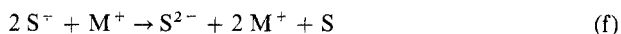


TABLE 1. SUBSTRATES REDUCED TO LI RADICAL ANIONS BY TREATMENT WITH LI METAL<sup>a</sup>

Substrate	Solvent	Characterization	Ref.
$C_6H_6$	THF	Alkylation	9
$C_6H_5NO_2$	THF	Isolated solid <sup>b</sup>	10
	HMPA	ESR	11
$C_6H_5C_6H_5$	Tetrahydropyran	Isolated crystal <sup>c</sup>	11
	THF		13
$C_{10}H_8^d$	THF	UV–VIS light	14
$C_{14}H_{10}^e$	HMPA	UV–VIS light	8
$C_{14}H_{10}^f$	THF	UV–VIS light	14
$C_{12}H_8^g$	2-CH <sub>3</sub> -THF	ESR	15
$C_{13}H_{10}^h$	Several <sup>i</sup>	UV–VIS light, ESR	16
$C_6H_5CH=CHC_6H_5$	THF	UV–VIS light	6
$(C_6H_5)_2C=C(C_6H_5)_2$	THF, DME	UV–VIS light	17
$C_6H_5C\equiv CC_6H_5$	THF	UV–VIS light	18
$C_{20}H_{12}^j$	THF	UV–VIS light	19
$C_{12}H_{10}^k$	THF	ESR	20
$C_5H_5N^l$	Pyridine	ESR	21
2,4,6- $(C_6H_5)_3C_5H_2N^m$	THF	Isolated complex	22

<sup>a</sup> The products are [substrate]<sup>•-</sup> Li<sup>+</sup> unless noted.

<sup>b</sup> The salt contains 50% of the expected radicals by magnetic susceptibility measurements.

<sup>c</sup> The crystal is isolated as a pentasolvate.

<sup>d</sup> Naphthalene.

<sup>e</sup> Anthracene.

<sup>f</sup> Phenanthrene.

<sup>g</sup> Biphenylene (A in Fig. 1).

<sup>h</sup> Fluorene (B in Fig. 1). Substituted fluorenes are also reduced to Li radical anions

<sup>i</sup> The radical anion is prepared in THF, DME, 2-Me-THF and tetrahydropyran.

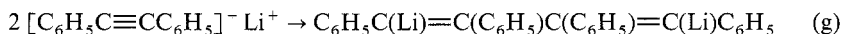
<sup>j</sup> Perylene (C in Fig. 1).

<sup>k</sup> Heptalene (D in Fig. 1).

<sup>l</sup> Pyridine; the product formed is Li 4,4'-bipyridine radical anion.

<sup>m</sup> 2,4,6-Triphenylpyridine.

where S is  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$ , is a function of solvent as well as the identity of the counterion and the concentration<sup>6</sup>. For  $\text{M} = \text{Li}$ , a change in solvent from ether to THF changes the equilibrium constant by more than six orders of magnitude. Radical anions are stabilized more by an increase in solvent donor ability than are dianions; e.g., the radical anion dimerization:



that proceeds in most ethers<sup>7</sup> does not occur<sup>8</sup> in HMPA.

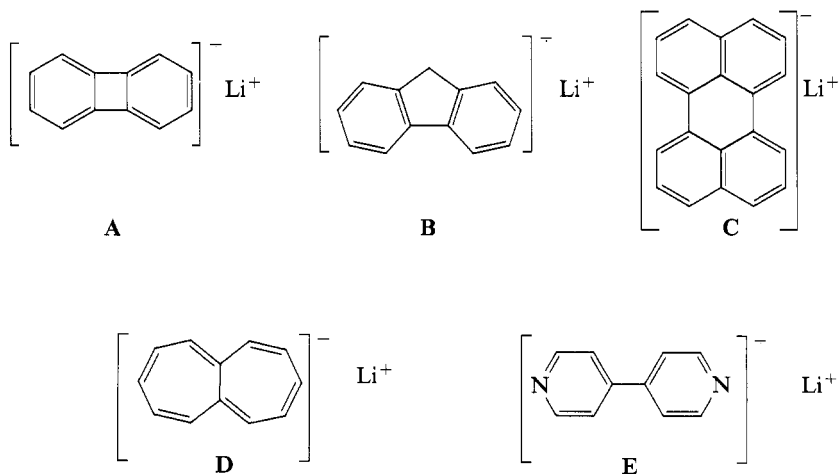
A discussion of Li metal and the atmospheres appropriate for the synthesis of organolithiums is given in the introduction to §5.5.2.2.1.

The delocalized radical anions and dianions formed in the reductions of Eqs. (a) and (b) are difficult to characterize. Derivatization, by either protonation or alkylation, may lead to mixtures of products, but UV-VIS, ESR and NMR spectroscopies can be useful. It is especially difficult to determine yields. In this section only preparations are used in which the organolithiums are characterized clearly unless the limits of the methods are being illustrated and few examples are available.

(i) Li Radical Anions<sup>1,3</sup>. Reduction of a substrate with 1 mol equiv of Li metal can produce a Li radical anion if the equilibrium constant for the disproportionation of Eq. (e) is small. For aromatic substrates not highly conjugated, the corresponding Li radical anions can be isolated in reasonable yields.

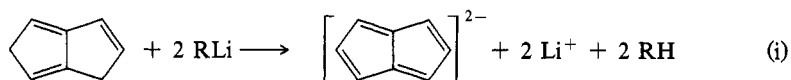
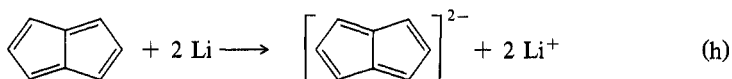
Table 1 lists preparations of Li radical anions, some of which are shown in Fig. 1. In addition to these, the ESR spectra of several polycyclic Li aromatic radical anions are recorded during the preparations of dilithium dianions discussed in subsection (ii).

(ii) Dilithium Dianions<sup>23</sup>. Treatment of conjugated organics with xs Li metal can give dilithium dianions according to Eqs. (a) and (b). In addition, the treatment of a conjugated organics with only 1 mol equiv of Li can lead to 50% conversion to a dilithium dianion if the equilibrium constant for Eq. (e) is large.



**Figure 1.** Lithium radical anions; see Table 1 for refs. Lithium radical anions of (A) biphenylene, (B) fluorene, (C) perylene, (D) heptalene and (E) 4,4'-bipyridine.

The formation of a dilithium dianion by the two-step reduction sequence gives the same product that would be formed by double deprotonation of a dihydro substrate, e.g., for pentalene:



Double deprotonations (see §5.5.2.3.2), exemplified by Eq. (i)<sup>24</sup>, are successful where the reduction according to Eq. (h) is not possible; e.g., for pentalene itself the reduction of Eq. (h) is not known.

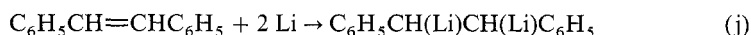
Because the dilithium dianions are formed from conjugated organics, these products are not well represented by localized structures. Similar to Li radical anions, the products discussed herein are represented as  $\text{R}^{2-} + 2 \text{Li}^+$ . Nevertheless, localized structures should be considered in which the Li atoms are bonded to the atoms that have the largest coefficients in the lowest energy antibonding orbital of the neutral precursor. Such a picture, when applicable, predicts reactivity in electrophilic substitution reactions of these dilithium dianions.

Dilithium dianions are easier to characterize than Li radical anions, and some are useful synthetic intermediates. However, electrophilic substitution can lead to mixtures. Dilithium dianions sometimes can be characterized by NMR spectroscopy.

Reduction of organic substrates to dianions can be divided into (a) reductions of polycyclic aromatics, (b) reductions of aryl-substituted alkenes or alkynes, (c) reductions of  $4n$   $\pi$ -electron systems, and (d) reduction of aryl ketones and derivatives.

Polycyclic aromatics that have low reduction potentials<sup>2</sup> are reduced by Li to give dilithium dianions. Among the more difficult to reduce members of this class that can react with Li are biphenyl<sup>13,25</sup> and naphthalene<sup>14,26,27</sup>. Other substrates that are reduced to dilithium dianions are shown in Fig. 2. In addition, several benzo-, dibenzo- and tribenzoanthracenes and larger polycyclic aromatic compounds are reduced to dilithium dianions<sup>28,29</sup>.

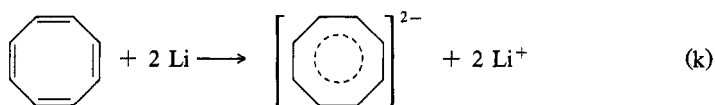
The reduction of an aryl-substituted alkene or alkyne by Li metal to give a dilithium dianion is similar to the reduction of a polycyclic aromatic compound. The products are represented by localized structures in which a C–C bond is reduced, e.g., in stilbene:



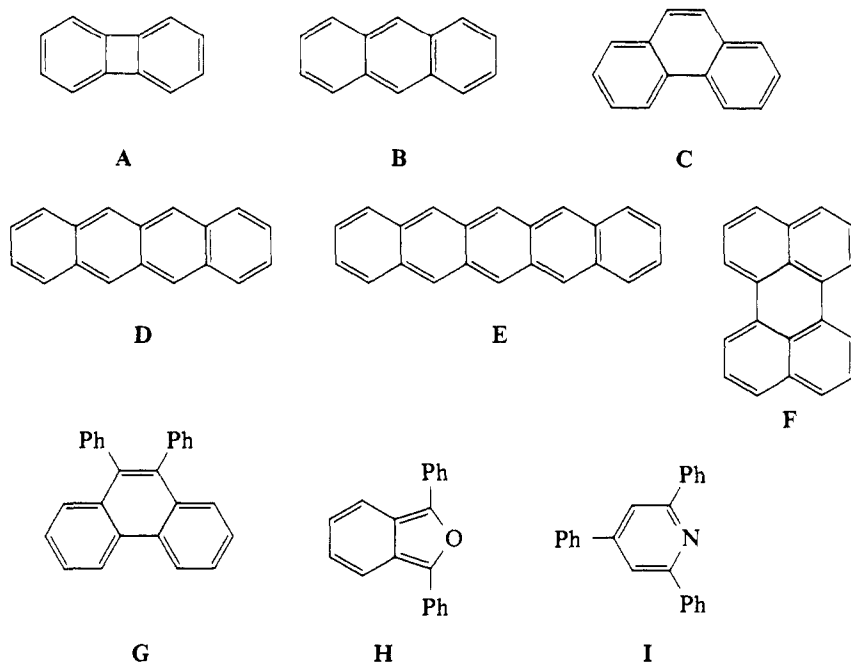
Examples of dilithium dianions in this group are collected in Table 2, where the products are represented with localized structures.

Lithium atoms produced in a metal-atom reactor react with simple alkenes at 700–800°C to give mixtures of dilithiobutenes in low yield<sup>37</sup>.

When  $4n$   $\pi$ -electron compounds are reduced to dilithium dianions, the resulting products contain  $(4n + 2)$   $\pi$  electrons and are aromatic as reflected in their NMR spectra; e.g., the reduction of cyclooctatetraene gives the 10  $\pi$ -electron dianion:





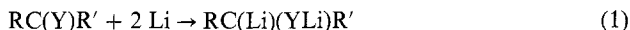


**Figure 2.** Aromatic compounds reduced to dilithium dianions: (A) biphenylene<sup>29</sup>, (B) anthracene<sup>29,30</sup>, (C) phenanthrene<sup>14,25</sup>, (D) naphthacene<sup>29</sup>, (E) pentacene<sup>27</sup>, (F) perylene<sup>29</sup>, (G) 9,10-diphenylphenanthrene<sup>25</sup>, (H) 2,5-diphenylisobenzofuran<sup>31</sup>, (I) 2,4,6-triphenylpyridine<sup>22</sup>.

The dilithium reagents from such reactions are represented poorly by localized structures and give mixtures of products on electrophilic substitution.

Figure 3 shows  $4n$   $\pi$ -electron and related species that are reduced to dilithium dianions. The dilithium dianions are produced in THF and characterized by NMR spectroscopy. The dilithium cyclooctatetraene dianion, however, gives 80% yield of dicarboxylic acids<sup>38</sup> when treated with  $\text{CO}_2$ .

Treatment of aryl ketones and their derivatives with Li results in dilithium species that are represented as adducts of Li to the carbon–heteroatom double bond:



where if  $\text{R} = \text{R}' = \text{C}_6\text{H}_5$ ,  $\text{Y} = \text{O}$ <sup>46,47</sup>; if  $\text{R} = \text{C}_6\text{H}_5$  and  $\text{R}' = \text{c-C}_6\text{H}_{11}$ ,  $\text{Y} = \text{O}$ <sup>48</sup>; if  $\text{R} = \text{R}' = \text{C}_6\text{H}_5$ ,  $\text{Y} = \text{NC}_6\text{H}_5$ <sup>49</sup>. A limited number of examples are known.

(iii) **Related Polyanion Formation.** Several reactions analogous to those in subsection (ii) involve substrates already containing C–Li bonds. The products, therefore, are polylithium species<sup>23</sup>. As in the examples above, two Li atoms formally add across a carbon–carbon multiple bond.

The trillithio species can be formed<sup>50</sup> in 95% yield as determined by treatment of the product with  $\text{D}_2\text{O}$ :

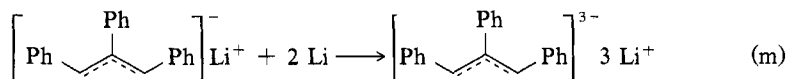
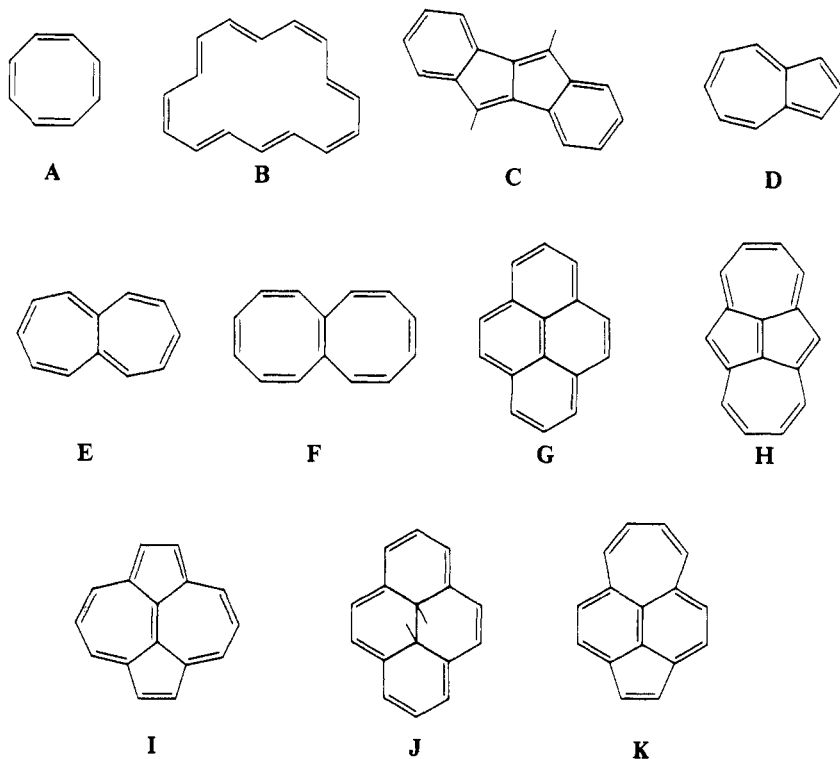


TABLE 2. DI-LITHIUM DIANIONS BY TREATMENT OF OLEFINS WITH LI METAL

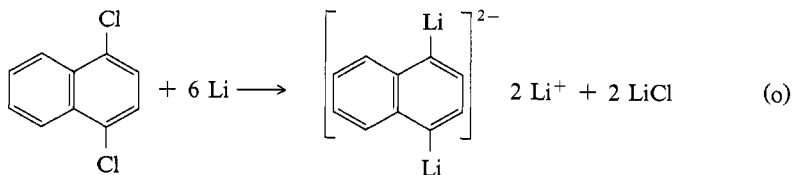
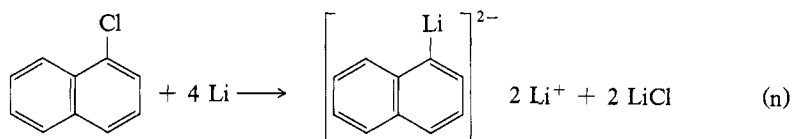
Substrate <sup>a</sup>	$[R]^{2-} 2 Li^+$	Solvent	Characterization	Refs.
$PhCH = CHPh$	$PhCH(Li)CH(Li)Ph$	THF	NMR	6,32
		Ether	UV-VIS light	6
		2-Me-THF <sup>b</sup>	UV-VIS light	6
		DME	Carboxylation	33
$PhCH = C(Ph)CH_3$	$PhCH(Li)C(Ph)(Li)CH_3$	THF	Protonation	34
$Ph_2C = CPh_2$	$Ph_2C(Li)C(Li)Ph_2$	THF	NMR	32
		DME, THF	UV-VIS light	17
$PhCH = CHCH = CHPh$	$PhCH(Li)CH = CHCH(Li)Ph$	THF	NMR	32
$PhCH = C(Ph)C(Ph) = CHPh$	$PhCH(Li)C(Ph) = C(Ph)CH(Li)Ph$	THF	Substitution	35
$PhC \equiv CHCH = C(Ph)SiMe_2^c$	$PhC(Li)CH = CHC(Li)(Ph)SiMe_2$	THF	NMR	32
$PhC \equiv C(Ph)C(Ph) = C(Ph)SiMe_2^d$	$PhC(Li)C(Ph) = C(Ph)C(Li)(Ph)SiMe_2$	THF	NMR	32
$C_{12}H_8^e$	$C_{12}H_8Li_2^f$	THF	Substitution	29,36
$PhC \equiv CPh$	$PhC(Li) = C(Li)Ph$	THF	Isolated precipitate	18

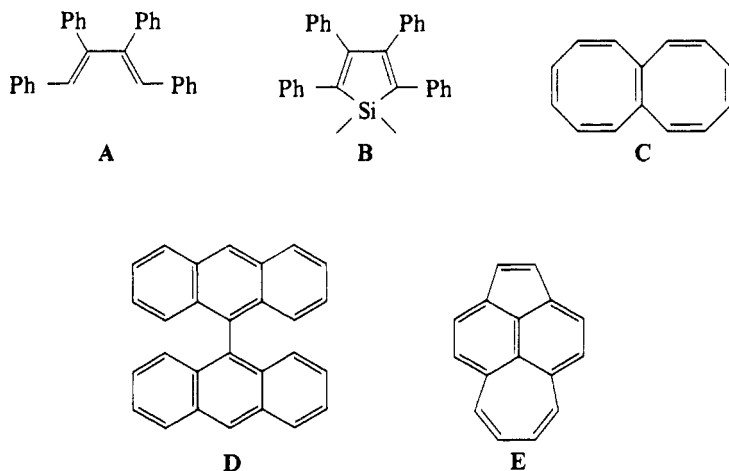
<sup>a</sup>  $Ph = C_6H_5$ ,  $Me \approx CH_3$ <sup>b</sup> 2-Me-THF = 2-methyltetrahydrofuran<sup>c</sup> 1,4-Diphenyl-5,5-dimethyl-5-silacyclopentadiene<sup>d</sup> 1,2,3,4-Tetraphenyl-5,5-dimethyl-5-silacyclopentadiene<sup>e</sup> Acenaphthylene<sup>f</sup> 1,2-Dithio-1,2-dihydroacenaphthylene



**Figure 3.** Some 4n π-electron and related compounds reduced to dilithium dianions: (A) cyclooctatetraene<sup>29,38,39</sup>, (B) 16-annulene<sup>40,41</sup>, (C) 1,9-dimethyldibenzo[b,f]pentalene<sup>42</sup>, (D) azulene<sup>29</sup>, (E) heptalene<sup>20</sup>, (F) octalene<sup>43</sup>, (G) pyrene<sup>29,44</sup>, (H) bis(cyclohepta)[cd,gh]pentalene<sup>44</sup>, (I) bis(cyclopenta)[ef,kl]heptalene<sup>44</sup>, (J) 15,16-dimethyl-15,16-dihydropyrene<sup>29</sup>, (K) acepleiadylene<sup>45</sup>.

The tri- and tetralithio products<sup>26</sup>:





**Figure 4.** Substrates that can react with four atoms of Li to give tetralithium tetraanions: (A) 1,2,3,4-tetraphenyl-1,3-butadiene<sup>35</sup>, (B) 5,5-dimethyl-1,2,3,4-tetraphenyl-5-silacyclopentadiene<sup>32</sup>, (C) octalene<sup>43</sup>, (D) 9,9'-bianthryl<sup>52</sup>, (E) acepleiadylene<sup>45</sup>.

illustrate why polycyclic aromatic halides cannot be converted to simple aryllithiums by Li metal.

The addition of four Li atoms to conjugated systems gives the tetralithium tetraanions in Fig. 4, as implied by NMR spectroscopy and derivatization. Tetralithium tetraanions are known from annulenes<sup>51</sup>.

(iv) Dilithium Dianions Formed by the Coupling of Li Radical Anions. The dimerization of Li radical anions, Eq. (d), is observed with Li radical anions formed from conjugated olefins. The products formed can be represented with localized structures (see Table 3). In addition to the stable dilithium species in Table 3, in situ trapping with  $(\text{CH}_3)_3\text{SiCl}$  of the products formed from the reaction of  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$  with Li gives  $(\text{CH}_3)_3\text{SiCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Si}(\text{CH}_3)_3$  in high yield<sup>53</sup>.

**TABLE 3. DILITHIUM DIANIONS BY DIMERIZATION OF LI RADICAL ANIONS**

Substrate <sup>a</sup>	$[\text{R}]^2- 2 \text{ Li}^+$	Solvent	Refs.
$\text{H}_2\text{C}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$	$\text{LiCH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2\text{Li}$	Ether	54
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$	$(\text{C}_6\text{H}_5)_2\text{C}(\text{Li})\text{CH}_2\text{CH}_2\text{C}(\text{Li})(\text{C}_6\text{H}_5)_2$	THF	55
		Anisole–benzene	56
$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{C}(\text{Li})=\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)=\text{C}(\text{Li})\text{C}_6\text{H}_5^b$	Ether	7
$(\text{C}_6\text{H}_5)_3\text{SiCH}=\text{CH}_2$	$(\text{C}_6\text{H}_5)_3\text{SiCH}(\text{Li})\text{CH}_2\text{CH}_2\text{CH}(\text{Li})\text{Si}(\text{C}_6\text{H}_5)_3^c$	THF	57,58

<sup>a</sup> Me =  $\text{CH}_3$ .

<sup>b</sup> Obtained in 65% yield.

<sup>c</sup> Obtained in 62% yield.

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#### 5.5.2.2.4. with Acidic Hydrocarbons Evolving H<sub>2</sub>.

**Organolithium solutions are pyrophoric and should be handled with care.**

Lithium metal may react with acidic hydrocarbons to give organolithiums. This reaction also occurs with other alkali metals, more commonly with the heavier group-IA metals potassium and Cs (see §5.5.3.2.4). Usually, deprotonation of acidic hydrocarbons (§5.5.2.3.2) is the method of choice for organolithiums from acidic hydrocarbons, but in special cases where contaminants must be avoided, the direct reaction with Li metal can be useful.

The reaction of Li metal with hydrocarbon acids is:

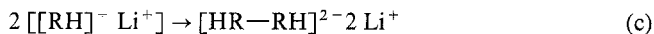


However, H<sub>2</sub> is not always evolved in these reactions.

The mechanisms are complex, and byproducts may arise in some pathways; e.g., a maximum yield of only 50 % of RLi is obtained by formation of the Li radical anion:



followed by coupling to give the dimeric dilithium dianion:



The dianion can serve as a base for deprotonation of the substrate:



The choice of pathways may be affected by the solvent and cation identity, e.g., in the treatment of 1,2-diphenylpropene with alkali metals<sup>1</sup>.

Yet other reaction pathways may be involved in reaction (a). Fluorene, e.g., is reduced<sup>2</sup> to a radical anion by Li metal at low T. When fluorene is treated with a limited amount of Li metal, fluorenyllithium is formed with no evolution of H<sub>2</sub> gas, but tetrahydro- and hexahydrofluorenes are produced<sup>3</sup>.

The synthesis of organolithiums according to Eq. (a) occurs in polar, aprotic solvents, such as tetrahydrofuran (THF), dimethoxyethane (DME) and hexamethylphosphoric triamide (HMPA). **Hexamethylphosphoric triamide causes tumors<sup>4</sup> and should be handled in a hood with appropriate protective measures.**

A discussion of Li metal and the atmospheres appropriate for the synthesis of organolithiums is contained in the introduction to §5.5.2.2.1.

Examples of organolithiums prepared by reaction of Li metal with an acidic hydrocarbon are presented in Table 1, along with those that form high yields of reduced dimeric substrate as byproducts. This procedure forms low yields of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CLi, and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub> fails to react with Li in DME. For practical purposes, therefore, the reaction should be attempted only with a hydrocarbon that has a pK<sub>a</sub> < 30.

26      5.5. Formation of Bonds between Elements of Groups IVB and IA  
           5.5.2. Carbon–Lithium Bonds  
           5.5.2.2. from Lithium and Its Alloys

53. D. R. Weyenberg, L. H. Toporcer, A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965).  
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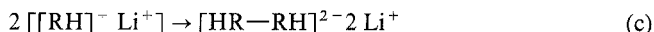


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followed by coupling to give the dimeric dilithium dianion:



The dianion can serve as a base for deprotonation of the substrate:



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Yet other reaction pathways may be involved in reaction (a). Fluorene, e.g., is reduced<sup>2</sup> to a radical anion by Li metal at low T. When fluorene is treated with a limited amount of Li metal, fluorenyllithium is formed with no evolution of H<sub>2</sub> gas, but tetrahydro- and hexahydrofluorenes are produced<sup>3</sup>.

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A discussion of Li metal and the atmospheres appropriate for the synthesis of organolithiums is contained in the introduction to §5.5.2.2.1.

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TABLE 1. ORGANOLITHIUMS FROM LITHIUM METAL WITH ACIDIC HYDROCARBONS

RLi	Solvent	Yield (%)	Refs.
C <sub>5</sub> H <sub>5</sub> Li <sup>a</sup>	THF	100	5
C <sub>9</sub> H <sub>7</sub> Li <sup>b</sup>	THF, DME	<sup>c</sup>	6
C <sub>13</sub> H <sub>9</sub> Li <sup>d</sup>	Ether, THF, DME, HMPA	<sup>c</sup>	6
	Ether, THF, DME	70–90	7
	2-Me-THF <sup>e</sup> , THF, DME	<sup>c</sup>	8
9-(C <sub>6</sub> H <sub>5</sub> )C <sub>13</sub> H <sub>8</sub> Li <sup>f</sup>	THF	38	9
C <sub>15</sub> H <sub>9</sub> Li <sup>g</sup>	THF	<sup>c,h</sup>	10
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CLi	DME	10 <sup>i</sup>	7
	THF	0	9
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHLi	DME	0 <sup>i</sup>	7
C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> Li	THF, DME	<sup>c</sup>	6
C <sub>6</sub> H <sub>5</sub> CH=CHCH(Li)C <sub>6</sub> H <sub>5</sub>	THF	<sup>c,j</sup>	11,12
CH <sub>2</sub> =CHCH=CHCH <sub>2</sub> Li <sup>k</sup>	THF + tertiary amine <sup>l</sup>	25–45 <sup>m</sup>	13

<sup>a</sup> Cyclopentadienyllithium.

<sup>b</sup> Indenyllithium.

<sup>c</sup> Not available.

<sup>d</sup> Fluorenyllithium.

<sup>e</sup> 2-Me-THF = 2-methyltetrahydrofuran.

<sup>f</sup> 9-Phenylfluorenyllithium.

<sup>g</sup> 4,5-Methylenepheneanthrenyllithium

<sup>h</sup> The product mixture, after protonation, contains ca. 25% yield of reduced substrate.

<sup>i</sup> The analogous reactions with potassium proceed to completion.

<sup>j</sup> The organolithium is contaminated with the reduced dimer, 1,4-diphenyl-2,3-dibenzylbutane.

<sup>k</sup> 1,3- or 1,4-Pentadiene serve as substrates.

<sup>l</sup> A tertiary amine, such as tetramethylethylenediamine, is required.

<sup>m</sup> The product is contaminated with a reduced dimer, C<sub>10</sub>H<sub>18</sub>.

In addition to the examples in Table 1, benzofluorenes<sup>10</sup> and ring-substituted fluorenes<sup>14</sup>, when treated with Li, give the corresponding organolithiums.

Acidic hydrocarbons, such as acetylene<sup>15</sup> and cyclopentadiene<sup>16</sup>, react with Li in liq NH<sub>3</sub> to give organolithiums, but these reactions may involve deprotonations by LiNH<sub>2</sub>.

Terminal olefins are reduced by Li metal to Li acetylides in ≤65% yield<sup>17</sup>:



where n = 0–3, 5, 7.

(M. E. NEWCOMB)

1. J. G. Smith, R. T. Wikman, *J. Organomet. Chem.*, **49**, 91 (1973).
2. D. Casson, B. J. Tabner, *J. Chem. Soc., B*, 887 (1969).
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17. D. L. Skinner, D. J. Peterson, T. J. Logan, *J. Org. Chem.*, 32, 105 (1967).

#### 5.5.2.2.5. with Ethers, Amines, Sulfides and Phosphines Cleaving the Carbon–Element Bonds.

**Organolithiums solutions are pyrophoric and should be handled with care.**

The cleavage of carbon–group-VIB, -VB or -IVB element bonds to give organolithiums is directly analogous to the Li cleavage of carbon–halogen bonds (see §5.5.2.2.1):



Application with the other group-IA metals is more common (see §5.5.3.2.1), but advances in the formation of alkyllithiums especially from alkylphenyl sulfides, suggest that reaction (a) will become a more popular synthetic tool. The application of reaction (a) instead of the corresponding reaction of Li metal with an organic halide is appropriate when the organic halide is so reactive that it couples with the organolithium, as for benzyl and allyl halides, or when other secondary reactions between the organic halide and the organolithium occur, as for tertiary halides.

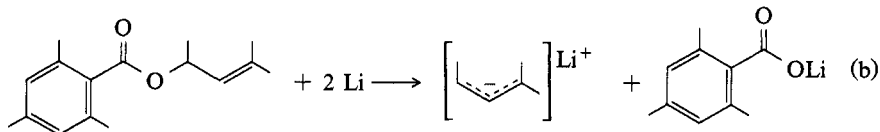
For reaction (a) to proceed, the Y group must form a stable Li salt. The reactivity of a carbon–element bond in Eq. (a) may be estimated by the acidity of the acid, HY. Therefore, the ease of cleaving representative substrates by Li rank<sup>1</sup>:  $RCl > RSC_6H_5 > ROC_6H_5 > RP(C_6H_5)_2$ . However, even C–C bonds can be cleaved by Li when both carbon atoms contain electron-withdrawing groups.

The Li-metal cleavages of Eq. (a) require strenuous conditions, and the organolithiums formed may attack the solvent subsequently. Tetrahydrofuran (THF) is the most efficacious, permitting less severe conditions. Excess Li metal is used.

A discussion of Li metal and the solvents and atmospheres appropriate for the synthesis of organolithiums appears in the introduction to §5.5.2.2.1.

(i) **Cleavage of Ethers.** Reaction of ethers with Li metal is employed when the corresponding organic halide is so reactive that it will couple with the organolithium. Benzylic and allylic Li reagents, e.g., can be prepared in high yield (see Table 1). The solutions of organolithiums produced contain Li alkoxides, which may alter reactivity and can interfere with spectroscopic studies.

In a related reaction that has synthetic potential, mesitoates may be cleaved by Li metal to give alkyllithiums<sup>9</sup>:



The reaction is useful only when the allyllithium is produced with a trapping agent in situ. The mesitoates may be prepared from allyl alcohols.

(ii) **Cleavage of Phenyl Sulfides.** Organolithiums form from sulfides with Li metal:



28      5.5. Formation of Bonds between Elements of Groups IVB and IA  
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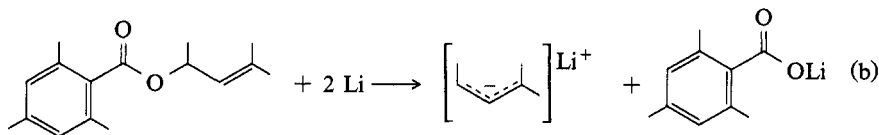
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(ii) **Cleavage of Phenyl Sulfides.** Organolithiums form from sulfides with Li metal:



TABLE 1. ORGANOLITHIUMS PREPARED FROM CLEAVAGE OF ETHERS BY LI METAL IN THF

Ether	RLi	T (°C)	Yield (%)	Refs.
$\text{RCH}=\text{CHCH}_2\text{OC}_6\text{H}_5^a$	$\text{RCH}=\text{CHCH}_2\text{Li}^a$	-15	65-80	2-4
$\text{RC}(\text{CH}_3)=\text{CHCH}_2\text{OC}_6\text{H}_5^b$	$\text{RC}(\text{CH}_3)=\text{CHCH}_2\text{Li}^b$	25	65	5
$\text{C}_6\text{H}_5\text{CH}_2\text{OR}^{c,d}$	$\text{C}_6\text{H}_5\text{CH}_2\text{Li}$	-10	75-83	6,7
$[\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)]_2\text{O}$	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Li}$	-10	65	7
$\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{OCH}_3\text{-h}^5^e$	$\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{Li-h}^5^f$	-5	80	8

<sup>a</sup> R = H, CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>.<sup>b</sup> R = H, CH<sub>3</sub>.<sup>c</sup> R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.<sup>d</sup> The solvent is THF-ether (2 : 1); C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Li is appreciably more soluble in this mixture than in THF.<sup>e</sup> Ferrocenylmethyl methyl ether.<sup>f</sup> Ferrocenylmethyl lithium.

Phenyl sulfides are more reactive than ethers, yet the sulfide precursors do not couple with organolithiums.

Because of the variety of phenyl sulfides, numerous precursors for organolithiums are available. Primary alkylphenyl sulfides are available from nucleophilic displacements of halides or addition of C<sub>6</sub>H<sub>5</sub>SH to terminal alkenes so that the sulfide hydrogen goes to the carbon with least hydrogens<sup>1</sup>. Secondary and tertiary alkylphenyl sulfides are available from addition of C<sub>6</sub>H<sub>5</sub>SH to alkenes in the reverse manner<sup>10</sup>. Alkoxyphenyl sulfides can be prepared also<sup>11</sup>. Other heteroatom-substituted phenyl sulfides, including phenylthioacetals<sup>12</sup> and ketene phenylthioacetals<sup>13</sup>, are also available.

The phenyl sulfides available permit the synthesis of organolithium by reaction (c) (see Table 2), e.g., tertiary alkylolithiums that are not available from the corresponding halides and sulfur-stabilized vinylolithiums that serve synthetically as acyl anion equivalents. Also, the benzyl ether moiety is not cleaved when the substrate contains both this moiety and a thiophenol group, and bis(phenyl sulfides) may be treated with 1-2 equiv of Li metal to give the mono- or dilithiums, respectively.

The organolithiums prepared by the cleavage of phenyl sulfides are contaminated with LiSC<sub>6</sub>H<sub>5</sub>, which may affect their reactivity. In synthetic reactions, however, the byproduct C<sub>6</sub>H<sub>5</sub>SH, which has a pK<sub>a</sub> of 6.5, is removed.

In several preparations in Table 2, a catalytic amount of naphthalene is added to the reaction, and in many a stoichiometric aromatic radical anion is employed. The aromatic compounds, via their radical anions, serve as transfer agents for Li, permitting the reactions to be run at lower T. Such procedures also allow use of a stoichiometric amount of Li metal, preventing overreduction in the case of bifunctional substrates. The presence of the aromatic compound in the product mixture can lead to purification problems; however, use of an acid-soluble aromatic, such as 1-dimethylaminonaphthalene, simplifies purification.

(iii) Other Cleavage Reactions. Aromatic heterocycles may be cleaved by Li; e.g., dibenzofuran and dibenzothiophene react to give Li reagents in 20 and 45% yield, respectively<sup>16</sup>.

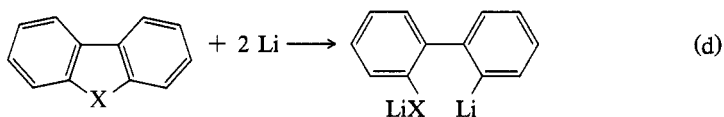


TABLE 2. ORGANOLITHIUMS IN THF FROM ALKYL- AND VINYLPHENYL SULFIDES WITH Li

RLi	Li type <sup>a</sup>	T (°C)	Yield (%)	Refs
$\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{Li}^b$	Li, cat	−20	87–93	1
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Li}$	Li, cat	−20	83	1
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$	Li	−20	79	1
$p\text{-(CH}_3\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Li}$	Li, cat	−20	71	1
$\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Li}$	Li, cat	−20	70	1
$\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{CH}_2\text{Li}$	Li, cat	−20	59	1
$p\text{-(LiCH}_2\text{CH}_2)_2\text{C}_6\text{H}_4$	Li	−20	94	1
$\text{LiCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Li}$	Li	−20	90	1
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Li}$	Li	−40	60	10
$\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{CH}_3)\text{Li}$	Li, cat	−40	78	10
$(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{Li}$	Li, cat	−40	50	10
$\text{CH}_2(\text{CH}_2)_4\text{CHLi}$	Li, Naph	−40	100	10
$(\text{CH}_3)_3\text{CLi}$	Li	−40	78	10
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Li}$	Li	−40	79	10
$(\text{C}_6\text{H}_5)_2\text{CHLi}$	Li	−40	90	10
$(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_3)\text{Li}$	Li	−40	93	10
$(\text{C}_6\text{H}_5)_2\text{CLi}$	Li	−40	92	10
$\text{LiCH}(\text{C}_6\text{H}_5)(\text{CH}_2)_4\text{CH}(\text{C}_6\text{H}_5)\text{Li}$	Li	−40	68	10
$\text{C}_6\text{H}_5\text{SCH}_2\text{Li}$	Li, Naph	−78	86	12
$\text{C}_6\text{H}_5\text{SCH}(\text{R})\text{Li}^c$	Li, Naph	−78	72–90	12
$\text{C}_6\text{H}_5\text{SCH}(\text{C}_6\text{H}_5)\text{Li}$	Li, Naph	−78	84	12
$(\text{CH}_3)_3\text{SiCH}(\text{R})\text{Li}^d$	Li, Naph	−78	80–86	12
$(\text{CH}_3)_3\text{SiC}(\text{Li})\text{CH}_2\text{CH}_2$	Li, Naph	−78	100	14
$\text{C}_6\text{H}_5\text{SC}(\text{Li})\text{CRR}'\text{CH}_2^e$	Li, Naph	−70	78–94	15
$(\text{CH}_3)_2\text{C}=\text{C}(\text{SC}_6\text{H}_5)\text{Li}$	Li, Naph	−70	77	13
$\text{CH}_2(\text{CH}_2)_4\text{CHCH}=\text{C}(\text{SC}_6\text{H}_5)\text{Li}$	Li, Naph	−70	68	13
$\text{CH}_2(\text{CH}_2)_4\text{C}=\text{C}(\text{SC}_6\text{H}_5)\text{Li}$	Li, Naph	−70	91	13
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OCH}_3)\text{Li}$	Li, Naph	−78	85	11
$(\text{CH}_3)_2\text{C}(\text{OCH}_3)\text{Li}$	LDMAN	−78	68	11
$\text{CH}_2(\text{CH}_2)_3\text{OCHLi}$	LDMAN	−78	64	11
$\text{CH}_3\text{OC}(\text{Li})\text{CH}_2\text{CH}_2$	LDMAN	−78	90	11
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{Li})\text{OSi}(\text{CH}_3)_3$	LDMAN	−78	88	11

<sup>a</sup> Li = metal; Li, cat = Li metal with a catalytic amount of naphthalene; Li, Naph = Li naphthalene radical anion; LDMAN = Li 1-dimethylaminonaphthalene radical anion.

<sup>b</sup> n = 5, 6.

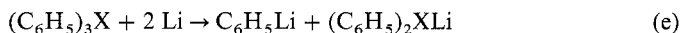
<sup>c</sup> R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>.

<sup>d</sup> R = H, CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>.

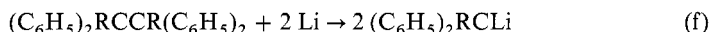
<sup>e</sup> R = R' = H; R = CH<sub>3</sub>, R' = H; R = R' = CH<sub>3</sub>.

Related heterocyclic ring openings occur, although the yields of organolithiums are often low, owing to secondary reactions with ethers<sup>17</sup>.

Cleavages of carbon-group-VB element bonds to give organolithiums occur with yields of  $C_6H_5Li$  (X, yield)<sup>18</sup>: N, 25; P, 64; As, 76; Sb, 62%. Usually, the Li salt of the group-VB element is the desired product, and the organolithium is a byproduct:



The cleavage of C—C bonds by Li to give organolithiums can occur also<sup>19,20</sup>, even when there is potential for C—O bond cleavage<sup>20</sup>:



where if R = H, the yield is 28% and if R =  $OC_6H_5$ , the yield is 89%.

Treatment of  $(C_6H_5)_2CHCl$  with Li produces  $(C_6H_5)_2CHLi$  via initial coupling followed by cleavage<sup>19</sup>. Similarly, Li metal cleaves 9,9-diphenylfluorene in THF to give 9-lithio-9-phenylfluorene in 85% yield<sup>21</sup>.

A related cleavage of the C—Si bond in  $C_6H_5CH_2Si(C_6H_5)_3$  gives  $C_6H_5CH_2Li$  in 18% yield<sup>22</sup>.

(M. E. NEWCOMB)

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### 5.5.2.3. from Other Organolithiums

#### 5.5.2.3.1. by Metal–Metal Exchange with Less Active Organometallics.

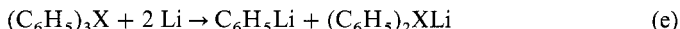
Transmetallations<sup>1,2</sup>:



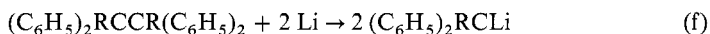
5.5. Formation of Bonds between Elements of Groups IVB and IA 31  
 5.5.2. Carbon–Lithium Bonds

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Transmetallations<sup>1,2</sup>:

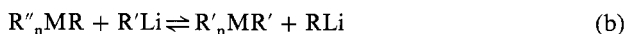


TABLE 1. TRANSMETALLATION EQUILIBRIA<sup>a</sup> IN Et<sub>2</sub>O

	% Ph <sub>4</sub> Sn	% cis- MeCH = CHLi <sup>a</sup>	% PhLi <sup>a</sup>
$(\text{cis-MeCH}=\text{CH})_4\text{Sn} + 4 \text{ PhLi} \xrightleftharpoons[(\text{ii})]{(\text{i})} \text{Ph}_4\text{Sn} + 4 \text{ cis-MeCH}=\text{CHLi}$			
Forward reaction (i)	50–56	49	29
Reverse reaction (ii)	51	46	25
$(\text{trans-MeCH}=\text{CH})_4\text{Sn} + 4 \text{ PhLi} \xrightleftharpoons[(\text{ii})]{(\text{i})} \text{Ph}_4\text{Sn} + 4 \text{ trans-MeCH}=\text{CHLi}$			
Forward reaction (i)	70–81	61	Not determined
Reverse reaction (ii)	79	69	20

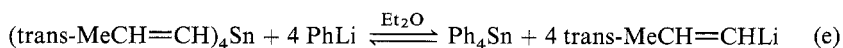
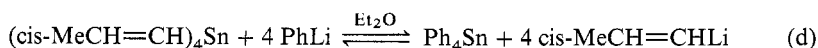
<sup>a</sup> After derivatization using Me<sub>3</sub>SiCl.

are routes to RLi that are difficult to prepare directly from RX (X = halide or H), as well as to RLi required free of LiX, LiOR or such donors as tetramethylethylenediamine (TMED).

Equations (a) and (b) are equilibria<sup>2–4</sup>, and exchange is realized from both directions for aryls<sup>3</sup>:



and for vinyls<sup>4</sup>:



See also Table 1.

Incomplete transmetalation, i.e., an equilibrium with two organolithiums in solution, can be disadvantageous; the more negative organic group provides the larger amount of organolithium in solution at equilibrium. Another factor leading to extensive formation<sup>5</sup> of organolithiums containing built-in donor centers is intra-aggregate complexation of the Li by the donor sites:



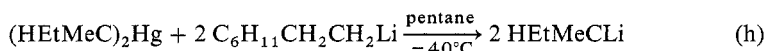
where X = alkoxy or amino and R' = alkyl.

Insolubility of one component can drive the exchange to one side as well as facilitate the isolation of a pure RLi, e.g.:



Organotins are most versatile, and organomercurials-, leads and -seleniums are also used widely.

Transmetalation is not useful in forming alkylolithiums, owing to unfavorable equilibria. Where exchanges of alkyl groups do occur, configuration is retained<sup>7</sup>:

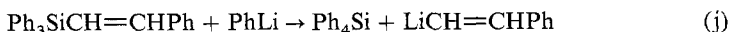


Both 1- and 2-alkenyl groups are transferred to Li (see below). When the double bond is more remote from the metal center, reactivity is reduced; e.g., 3-butenyl- and 4-pentenyltins do not exchange with *n*-BuLi in Et<sub>2</sub>O.

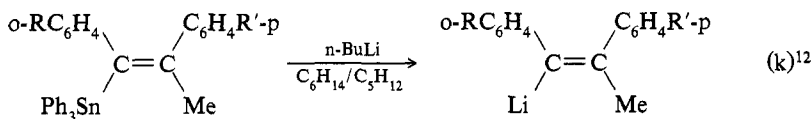
(i) Vinylolithiums. Vinylolithium is prepared from (CH<sub>2</sub>=CH)<sub>4</sub>Sn and PhLi in Et<sub>2</sub>O<sup>4</sup> or tetrahydrofuran (THF)<sup>8</sup>, from (CH<sub>2</sub>=CH)<sub>4</sub>Sn and *n*-BuLi in pentane or Et<sub>2</sub>O, from Ph<sub>3</sub>MCH=CH<sub>2</sub> (M = Sn or Pb) and PhLi and from (CH<sub>2</sub>=CH)<sub>4</sub>Pb and PhLi in Et<sub>2</sub>O<sup>9</sup>. By contrast, PhLi adds to Ph<sub>3</sub>MCH=CH<sub>2</sub>:



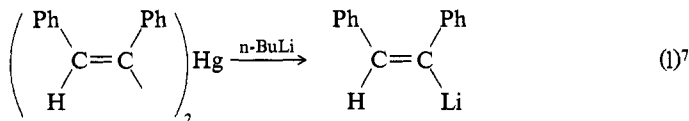
where M = Si<sup>10</sup> or Ge<sup>4</sup>. Changing the vinyl substituents can lead to transmetallation, even for vinylsilanes<sup>11</sup>:



As shown in Eqs. (d), (e) and (l)–(m) and in Table 2, transmetallations involving vinyl groups occur with retention of configuration:



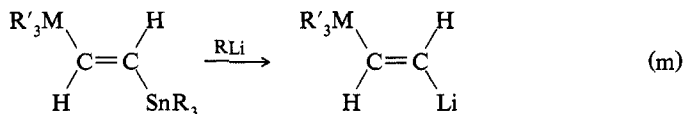
where R, R' = NMe<sub>2</sub>, H; CH<sub>2</sub>NMe<sub>2</sub>, Me; H, H.



For transmetallations involving R'Li (R' = alkyl or phenyl), the equilibrium, Eq. (a) or (b), lies farther to the product side in the sequence<sup>4</sup> MR = CH<sub>2</sub>=CHMeSn, trans-MeCH=CHSn, cis-MeCH=CHSn, CH<sub>2</sub>=CHSn. Thus only poor yields of CH<sub>2</sub>=CHMeLi are obtained from (CH<sub>2</sub>=CHMe)<sub>4</sub>Sn and PhLi (4 equiv) in Et<sub>2</sub>O. To gain good yields of trans-MeCH=CHLi from trans-MeCH=CHSnMe<sub>3</sub> in Et<sub>2</sub>O, 2 equiv of MeLi are recommended<sup>4</sup>.

Reactions proceed farther in Et<sub>2</sub>O than in hydrocarbons. Only partial exchange occurs between (CH<sub>2</sub>=CH)<sub>4</sub>Sn and *n*-BuLi in C<sub>5</sub>H<sub>12</sub>, in contrast to the complete transmetallation of all four groups in Et<sub>2</sub>O. Despite this, C<sub>5</sub>H<sub>12</sub> is a useful solvent for the reaction because CH<sub>2</sub>=CHLi is only partially soluble in it and can be isolated.

Reactions of trans-R'<sub>3</sub>MCH=CHSnR<sub>3</sub> (M = Si or Sn) with RLi provide trans-R'<sub>3</sub>MCH=CHLi in good yield:

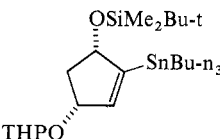
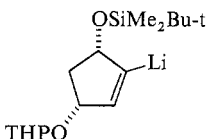
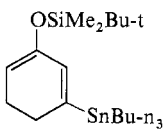
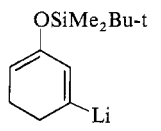
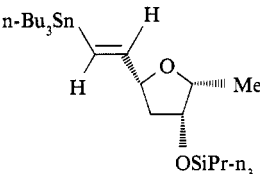
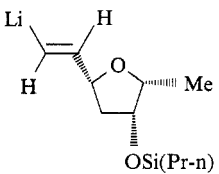


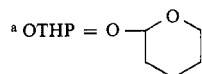
where if R = R' = *n*-Bu, M = Sn in THF at –78°C<sup>13,14</sup>; if R = R' = Ph, M = Sn in Et<sub>2</sub>O<sup>13</sup>; if R = *n*-Bu or Ph, R' = Me, M = Si<sup>15</sup>.

Use of 2 equiv of *n*-BuLi does not provide trans-LiCH=CHLi from trans-*n*-Bu<sub>3</sub>SnCH=CHSn(Bu-*n*)<sub>3</sub> (I); only the mono exchange product<sup>13</sup>, trans-*n*-Bu<sub>3</sub>SnCH=CHLi,



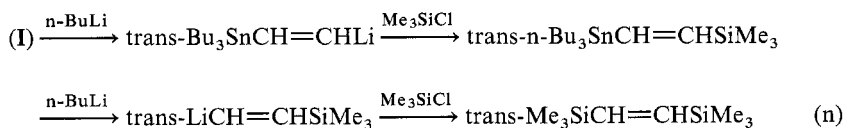
**TABLE 2.** TRANSMETALLATIONS INVOLVING VINYLINS OR VINYLSELENIUMS AND *n*-BUTYLLITHIUM:  
 $MCH=CHX + n-BuLi \rightarrow XCH=CHLi$ 

Vinyltin or Se	Conditions	Product	Refs.
(Z)-Bu <sub>2</sub> SnCH=CHNMePh	THF, -70°C	(Z)-LiCH=CHNMePh	19
(Z)-Bu <sub>2</sub> SnCH=CHOEt	THF, -78°C	(Z)-LiCH=CHOEt	19,20
n-Bu <sub>3</sub> SnCH=CHCH <sub>2</sub> OH, (Z) : (E) = 5 : 1	C <sub>5</sub> H <sub>12</sub> , -50°C	LiCH=CHCH <sub>2</sub> OLi	21
(E)-n-Bu <sub>3</sub> SnCH=CHCH <sub>2</sub> O <sup>a</sup>	THF, -78°C	(E)-LiCH=CHCH <sub>2</sub> O <sup>a</sup>	22
(E)-n-Bu <sub>3</sub> SnCH=CHCH <sub>2</sub> OCH <sub>2</sub> SMc	THF, -78°C	(E)-LiCH=CHCH <sub>2</sub> OCH <sub>2</sub> SMc	23
(E)-n-Bu <sub>3</sub> SnCH=CHCH(C <sub>5</sub> H <sub>11</sub> )- OSiEt <sub>3</sub>	THF, -50°C	(E)LiCH=CHCH(C <sub>5</sub> H <sub>11</sub> )- OSiEt <sub>3</sub>	24,25
n-Bu <sub>3</sub> SnCH=CHCH <sub>2</sub> CMe <sub>n</sub> - BuOSiMe <sub>3</sub> , (Z) : (E) = 1 : 10	THF, -35°C	LiCH=CHCH <sub>2</sub> CMe <sub>n</sub> BuOSiMe <sub>3</sub>	24,25
n-Bu <sub>3</sub> SnCH=CHCH <sub>2</sub> CHMeO <sup>a</sup> , (Z) : (E) = 3 : 17	THF, -78°C	LiCH=CHCH <sub>2</sub> CHMeO <sup>a</sup> THP <sup>a</sup>	26
	THF, -45°C		27
	THF, -78°C		28
n-Bu <sub>3</sub> SnCH=CHCH=CHOEt	THF, -78°C	LiCH=CHCH=CHOEt	29
Me <sub>3</sub> SnC(SPh)=CPh <sub>2</sub>	THF, -78°C	LiC(SPh)=CPh <sub>2</sub>	30
Me <sub>3</sub> SnC(SPh)=CH <sub>2</sub>	THF, -78°C	LiC(SPh)=CH <sub>2</sub>	30
Me <sub>3</sub> SnC(SPh)=CHPh	THF, -78°C	LiC(SPh)=CHPh	30
(PhSe) <sub>2</sub> C=CHPh	THF, -78°C	(E)-LiC(SePh)=CHPh	30
	THF, -78°C <sup>b</sup>		31
H <sub>2</sub> C=C(SnMe <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> Cl	THF, -78°C	H <sub>2</sub> C=CLi(CH <sub>2</sub> ) <sub>2</sub> Cl	32
H <sub>2</sub> C=C(SnMe <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> Cl	THF, -78°C	H <sub>2</sub> C=CLi(CH <sub>2</sub> ) <sub>3</sub> Cl	33
t-BuCH=C(SnMe <sub>3</sub> ) <sub>2</sub>	THF, -78°C <sup>b</sup>	(E)-t-BuCH=CLiSnMe <sub>3</sub>	34

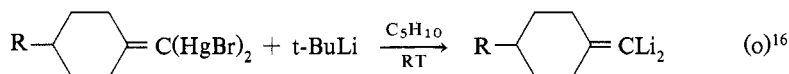


<sup>b</sup> MeLi used.

is obtained. Caution should be exercised when using  $\text{Me}_3\text{SiCl}$  as the derivatization agent to identify lithiated products. The formation of  $\text{trans-Me}_3\text{SiCH=CHSiMe}_3$  from (I) is not a result of the intermediacy of  $\text{LiCH=CHLi}$ , but a consequence of the sequence:

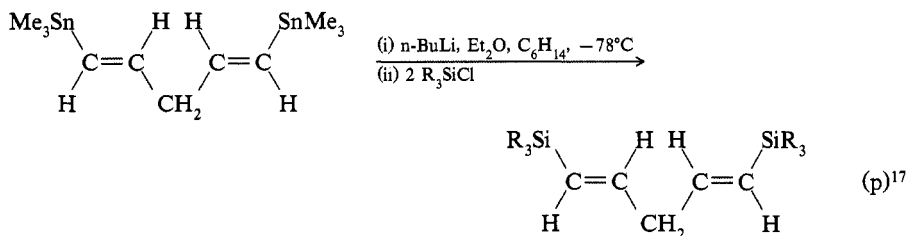


Other attempts to prepare dilithio derivatives via transmetalations of tin derivatives fail, e.g.,  $o\text{-(Me}_3\text{Sn)}_2\text{C}_6\text{H}_4$ ; from  $\text{RCH=C(SnMe}_3)_2$  as well as from  $\text{Ph}_3\text{SnCH=CHSnPh}_3$ <sup>13</sup> in each case only one  $\text{R}_3\text{Sn}$  group is replaced, even when  $\text{xSRLi}$  is used [see Eq. (bc), below]. However, dilithio derivatives are prepared from dimercurio compounds:

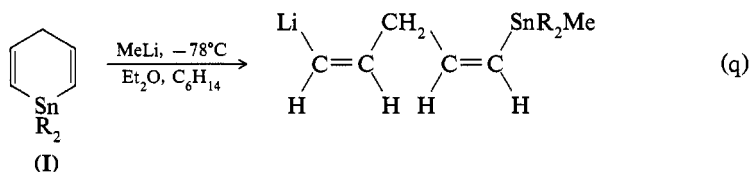


where  $\text{R} = \text{H}$  or  $t\text{-Bu}$ .

The compound  $(1\text{E}), (4\text{E})\text{-LiCH=CHCH}_2\text{CH=CHLi}$  is claimed from  $\text{Me}_3\text{Sn-CH=CHCH}_2\text{CH=CHSnMe}_3$  with  $n\text{-BuLi}$ . However, no lithiated species is identified; only derivatization by  $\text{R}_3\text{SiCl}$  is used:



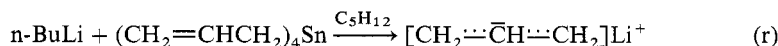
The tin heterocycle (I) is cleaved by  $\text{RLi}$ <sup>17</sup>:



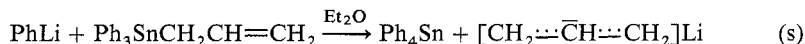
where  $\text{R} = \text{Me}$  or  $n\text{-Bu}$ . Trifluorovinyl lithium is prepared from  $n\text{-BuSn(CF=CF}_2)_3$  and  $n\text{-BuLi}$  in  $\text{Et}_2\text{O}$ , from  $(\text{CF}_2=\text{CF})_4\text{Sn}$  and  $\text{PhLi}$  in  $\text{Et}_2\text{O}$  at  $-40^\circ\text{C}$ , or from  $\text{PhSi(CF=CF}_2)_3$  in  $\text{Et}_2\text{O-pentane}$ <sup>18</sup>.

Other examples involving functionally substituted vinyl groups are listed in Table 2.

(ii) Allyllithiums. Allyllithium is prepared from<sup>35,36</sup>  $(\text{CH}_2=\text{CHCH}_2)_4\text{Sn}$  and  $n\text{-BuLi}$ :



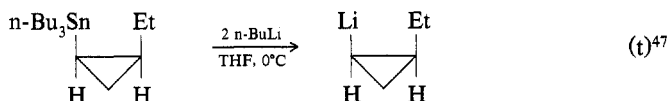
or from PhLi in pentane or Et<sub>2</sub>O, as well as from Ph<sub>3</sub>SnCH<sub>2</sub>CH=CH<sub>2</sub> and PhLi in Et<sub>2</sub>O:



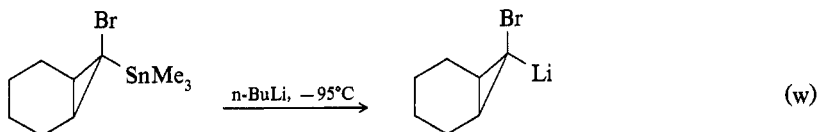
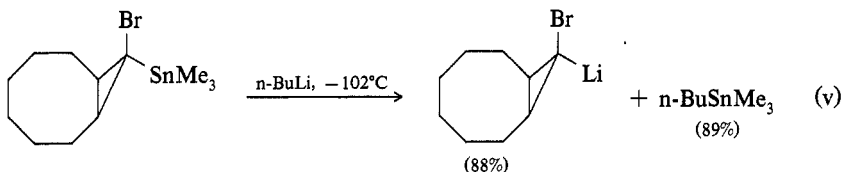
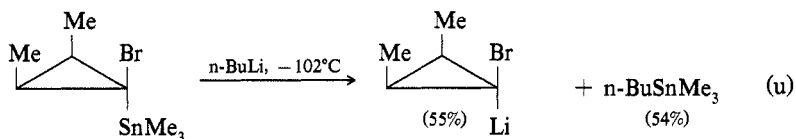
Allyl selenides, RR'C=CHCH<sub>2</sub>SeR'', are also used (see Table 3).

Table 3 lists substituted allyls prepared from organotin and -leads.

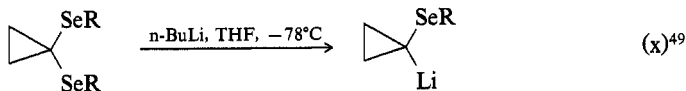
(iii) Cyclopropyllithiums. Good yields of cyclo-C<sub>3</sub>H<sub>5</sub>Li are obtained from 1:2 (cyclo-C<sub>3</sub>H<sub>5</sub>)<sub>4</sub>Sn and n-BuLi <sup>47</sup>:



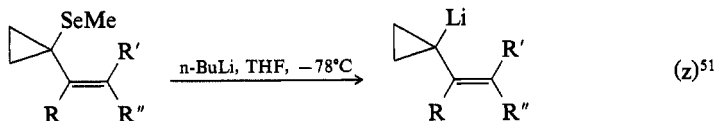
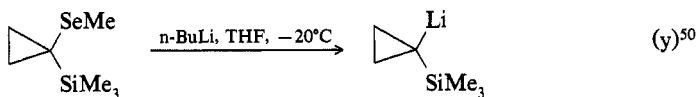
1-Halo-1-lithiocyclopanes also can be prepared by transmetallation<sup>48</sup>:



Cleavage of C—Se bonds also provides cyclopropyllithiums:



where R = Ph or Me;



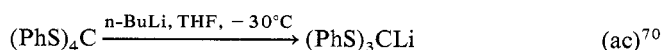
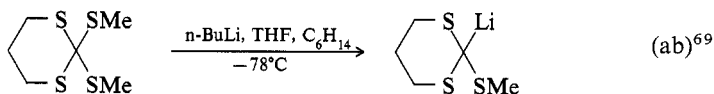
Metal Allyl	RLi	Conditions	Product	Refs.
$\text{H}_2\text{C}=\text{CHCH}_2\text{SePh}$	n-BuLi	THF, $-78^\circ\text{C}$	$[\text{H}_2\text{C} \cdots \bar{\text{C}}\text{H} \cdots \text{CCH}_2]\text{Li}^+$	37
$\text{MeCH}=\text{CHCH}_2\text{SnMe}_3$ , (Z) or (E)	MeLi	$\text{Et}_2\text{O}$ , RT	$[\text{MeCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	38
$\text{MeCH}=\text{CHCH}_2\text{SnPh}_3$	PhLi	$\text{Et}_2\text{O}$ , RT	$[\text{MeCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	38
$(\text{MeCH}=\text{CHCH}_2)_4\text{Sn}$	EtLi	PhH, RT	$[\text{MeCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	38
$\text{Me}_3\text{SnCH}_2\text{CH}=\text{CHC}_6\text{H}_{13}$ , (E):(Z) = 70:30	MeLi	THF, RT	$[\text{C}_6\text{H}_{13}\text{CH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}]\text{Li}^+$	39
$\text{Me}_3\text{SnCH}_2\text{CH}=\text{C}_6\text{H}_{11}$	MeLi	THF, RT	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{C}_6\text{H}_{11}]\text{Li}^+$	39
(E)- $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CHPh}$	MeLi	THF, RT	$[\text{PhCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	39
(E)- $\text{Me}_3\text{SnCH}_2\text{CMe}=\text{CHEt}$ , (E):(Z) = 1:1	MeLi	THF, RT	$[\text{EtCH} \cdots \text{CMe} \cdots \text{CH}_2]\text{Li}^+$	39
$\text{Me}_3\text{SnCH}_2\text{CH}=\text{CF}_2$	n-BuLi	THF, $-95^\circ\text{C}$	$[\text{CF}_2 \cdots \bar{\text{C}} \cdots \text{CH}_2]\text{Li}^+$	40
$\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CCl}_2$	n-BuLi	THF, $-95^\circ\text{C}$	$[\text{CCl}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	41–43
$\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CClSiMe}_3$	n-BuLi	THF, $-90^\circ\text{C}$	$[\text{Me}_3\text{SiCCl} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	44
$\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CHCl}$	n-BuLi	THF, $-90^\circ\text{C}$	$[\text{CHCl} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	45,46
$\text{Ph}_3\text{PbCH}_2\text{CH}=\text{CClMe}$	n-BuLi	THF, $-90^\circ\text{C}$	$[\text{MeCCl} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$	45

(iv)  $\alpha$ -Halo- and  $\alpha$ -Metallo-Substituted Alkylolithiums. Dimetallated methanes,  $R_nMCH_2M'R'_m$  ( $M, M' = As, Sb, Ge, Sn, Pb, Se, Te$ ), undergo monometallations to give monometallated methylolithiums<sup>52-56</sup>:



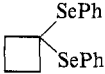
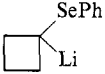
Tris-metallomethanes, e.g.,  $(\text{Ph}_3\text{Pb})_3\text{CH}$ <sup>56</sup>,  $(\text{Ph}_3\text{Pb})_2\text{CHAsPh}_2$ <sup>56</sup>,  $(\text{PhSe})_3\text{CH}$ , and tetra-kis-metallomethanes, e.g.,  $(\text{PhSe})_4\text{C}$ <sup>55</sup>, also undergo transmetalations (see Table 4). Seleno-substituted alkylolithiums are prepared by transmetalation<sup>53,54,57–61</sup>.

Tetrathioalkoxymethanes react similarly with RLi:

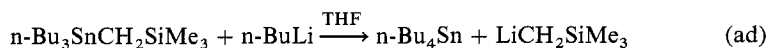


Unlike  $(\text{Ph}_3\text{Pb})_3\text{CH}$ ,  $(\text{Ph}_3\text{Sn})_3\text{CH}$  does not undergo transmetallation with *n*-BuLi;  $(\text{Ph}_2\text{M})_3\text{CH}$  (M = Sb or As) also do not readily undergo transmetallations<sup>56</sup> with *n*-BuLi.

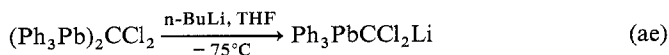
TABLE 4. FORMATION OF METALLOALKYLLITHIUMS

Polymetalloalkane	RLi	Conditions	Product	Refs.
$(\text{Ph}_3\text{Pb})_2\text{CH}_2$	PhLi	THF, $-70^\circ\text{C}$	$\text{Ph}_3\text{PbCH}_2\text{Li}$	52
$\text{Me}_3\text{SiCH}_2\text{SnBu-n}_3$	n-BuLi	THF, $0^\circ\text{C}$	$\text{Me}_3\text{SiCH}_2\text{Li}$	62
$\text{Ph}_3\text{PbCH}_2\text{GePh}_3$	PhLi	THF, $-70^\circ\text{C}$	$\text{Ph}_3\text{GeCH}_2\text{Li}$	52
$(\text{Ph}_3\text{Pb})_3\text{CH}$	PhLi		$(\text{Ph}_3\text{Pb})_2\text{CHLi}$	56
$(\text{Ph}_3\text{Pb})_2\text{CHSiMe}_3$	PhLi		$\text{Ph}_3\text{PbCHLi}(\text{SiMe}_3)$	56
$(\text{Ph}_3\text{Pb})_2\text{CHGePh}_3$	PhLi		$\text{Ph}_3\text{PbCHLi}(\text{GePh}_3)$	56
$(\text{Ph}_3\text{Pb})_2\text{CHAsPh}_2$	PhLi		$\text{Ph}_3\text{PbCHLi}(\text{AsPh}_2)$	56
$(\text{Ph}_3\text{Pb})_2\text{CCl}_2$	n-BuLi	THF, $\text{Et}_2\text{O}, \text{CH}_2(\text{OMe})_2$ , $\text{C}_5\text{H}_{12}$ , $-130^\circ\text{C}$	$\text{Ph}_3\text{PbCCl}_2\text{Li}$	63
$\text{Ph}_3\text{PbCCl}_2\text{HgPh}$	n-BuLi		$\text{Ph}_3\text{PbCCl}_2\text{Li}$	63
$(\text{Me}_3\text{Sn})_2\text{CCl}_2$	n-BuLi	THF, $-95^\circ\text{C}$	$\text{Me}_3\text{SnCCl}_2\text{Li}$	64
$(\text{Ph}_3\text{As})_2\text{CH}_2$	n-BuLi	THF, $-40^\circ\text{C}$	$\text{Ph}_2\text{AsCH}_2\text{Li}$	52
$(\text{Ph}_3\text{Sb})_2\text{CH}_2$	PhLi	THF, $-70^\circ\text{C}$	$\text{Ph}_2\text{SbCH}_2\text{Li}$	52
$(\text{PhSe})_2\text{CH}_2$	n-BuLi	THF, $-78^\circ\text{C}$	$\text{PhSeCH}_2\text{Li}$	53
$(\text{PhSe})_3\text{CMe}$	n-BuLi	THF, $-78^\circ\text{C}$	$(\text{PhSe})_2\text{CMeLi}$	54
$(\text{PhSe})_4\text{C}$	n-BuLi	THF, $-78^\circ\text{C}$	$(\text{PhSe})_3\text{CLi}$	54
$(\text{PhTe})_2\text{CH}_2$	n-BuLi	THF, $-78^\circ\text{C}$	$\text{PhTeCH}_2\text{Li}$	55
$\text{Me}_3\text{SiCH}(\text{C}_6\text{H}_{13})\text{Me}$	n-BuLi	THF, $0^\circ\text{C}$	$\text{Me}_3\text{SiCHC}_6\text{H}_{13}\text{Li}$	57
$\text{PhSCH}_2\text{SePh}$	n-BuLi	THF, $-78^\circ\text{C}$	$\text{PhSH}_2\text{Li}$	65
	n-BuLi	THF, $-78^\circ\text{C}$		66
$\text{BrHg}(\text{CH}_2)_3\text{HgBr}$	t-BuLi	$\text{C}_5\text{H}_{12}$	$\text{Li}(\text{CH}_2)_3\text{Li}$	67
$\text{CH}_2(\text{HgI})_2$	xs n-BuLi	$\text{C}_6\text{H}_{14}$	$\text{CH}_2\text{Li}_2$	68

No exchange occurs between n-BuLi and n-Bu<sub>3</sub>SnCH<sub>2</sub>SiMe<sub>3</sub> in hexane after 24 h at RT, and in the presence of TMED only 25% reaction results after 24 h<sup>71</sup>. By contrast, in THF, exchange is complete at  $0^\circ\text{C}$  within  $\frac{1}{2}$  h<sup>62</sup>:

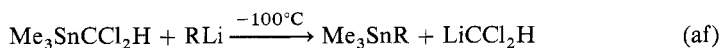


The reaction of  $(\text{Ph}_3\text{Pb})_2\text{CCl}_2$  with n-BuLi proceeds<sup>63</sup> at low T:

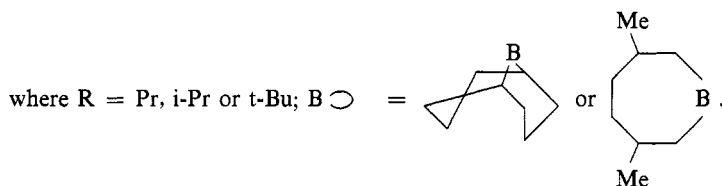
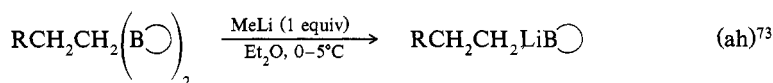
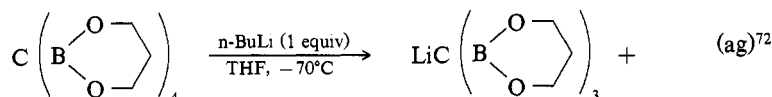


With  $\text{Ph}_3\text{PbCCl}_2\text{SnPh}_3$ , products of cleavage of either metal–carbon bond are obtained. For the Si and Ge derivatives,  $\text{Ph}_3\text{PbCCl}_2\text{MPh}_3$  (M = Si or Ge), C–Cl exchange and Pb–C cleavage occur on reaction with n-BuLi. Other reactions of dimetallodihalomethanes with n-BuLi are listed in Table 4.

Reaction of  $\text{Me}_3\text{SnCCl}_2\text{H}$  with  $\text{RLi}$  ( $\text{R} = n\text{-Bu}$  or  $t\text{-Bu}$ ) at  $-100^\circ\text{C}$  provides<sup>64</sup>  $\text{LiCCl}_2\text{H}$ :

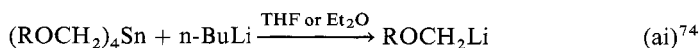


Di- and polyboroalkanes<sup>72,73</sup> are also cleaved by  $\text{RLi}$ :

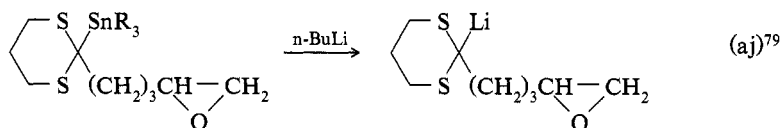


Di- and polythioalkanes are generated from the corresponding mercuriated precursors and alkyllithiums<sup>68,69</sup>.

$\alpha$ -Alkoxy-,  $\alpha$ -Thioalkoxy- or  $\alpha$ -Aminoalkyllithiums. Transmetalations occur between  $\text{RLi}$  and  $\alpha$ -alkoxy-<sup>4,71,74-78</sup>:



where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $i\text{-Pr}$  or  $\text{PhCH}_2$  (yield  $> 60\%$ );  $\alpha$ -thioalkoxy-<sup>71,79</sup>; or  $\alpha$ -amino-alkyltins<sup>71,80</sup> (see Table 5):



Transfer of  $\alpha$ -alkoxyorgano groups from  $\text{Sn}$  to  $\text{Li}$  occurs with retention of configuration<sup>76</sup>:

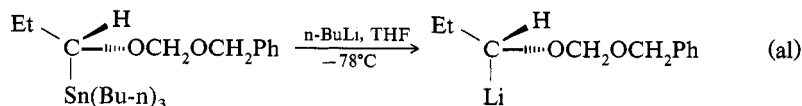


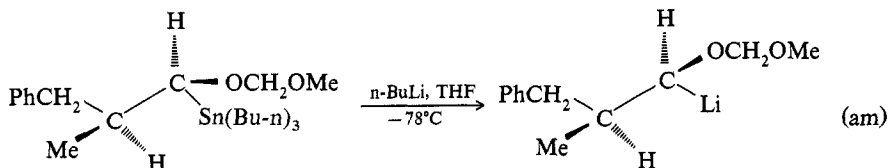


TABLE 5. TRANSMETALLATIONS INVOLVING  $\alpha$ -SUBSTITUTED ALKYLSTINS

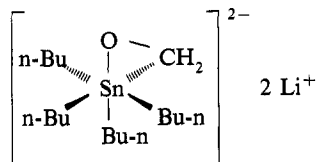
Tin compound	RLi	Conditions	Product	Refs.
$n\text{-Bu}_3\text{SnCH}_2\text{OMe}$	$n\text{-BuLi}$	Hexane	$\text{LiCH}_2\text{OMe}$	71
$n\text{-Bu}_3\text{SnCH(OMe)C}_6\text{H}_{13}$	$n\text{-BuLi}$	THF, $-70^\circ\text{C}$	$\text{LiCH(OMe)C}_6\text{H}_{13}$	75
$\text{Me}_3\text{SnCH}_2\text{OSiMe}_3$	$n\text{-BuLi}$	THF, $-80^\circ\text{C}$	$\text{LiCH}_2\text{OSiMe}_3$	78
$n\text{-Bu}_3\text{SnCH(R)OCHMeOEt}^a$	$n\text{-BuLi}$	THF, $-80^\circ\text{C}$	$\text{LiCH(R)OCHMeOEt}$	
$n\text{-BuCH[OCH}_2\text{Sn(Bu-}n\text{)}_3]$	$n\text{-BuLi}$	THF, $-78^\circ\text{C}$	$n\text{-BuCH(OCH}_2\text{Li)-CMe=CH}_2$	81
$2,4,6\text{-(i-Pr)}_3\text{C}_6\text{H}_2\text{CO}_2$	$\text{MeLi}$	THF, $-78^\circ\text{C}$	$\text{ArCO}_2\text{CHMeLi}^b$	82
$\text{CHMeSn(Bu-}n\text{)}_3$				
$n\text{-Bu}_3\text{SnCH}_2\text{SMe}$	$n\text{-BuLi}$	Hexane	$\text{LiCH}_2\text{SMe}$	71
$\text{Ph}_3\text{SnCH}_2\text{SC}_6\text{H}_4\text{Me-p}$	$n\text{-BuLi}$	Hexane	$\text{LiCH}_2\text{SC}_6\text{H}_4\text{Me-p}$	83
$n\text{-Bu}_3\text{SnCH}_2\text{NMe}_2$	$n\text{-BuLi}$	Hexane	$\text{LiCH}_2\text{NMe}_2$	71
$n\text{-Bu}_3\text{SnCH}_2\text{NMeCH}_2\text{Ph}$	$n\text{-BuLi}$	THF, $-65^\circ\text{C}$	$\text{LiCH}_2\text{NMeCH}_2\text{Ph}$	71
$n\text{-Bu}_3\text{SnCH}_2\text{NMe(CH}_2\text{CH}_2\text{OH)}$	$n\text{-BuLi}$	THF, $-65^\circ\text{C}$	$\text{LiCH}_2\text{NMe(CH}_2\text{CH}_2\text{OLi)}$	71
$n\text{-Bu}_3\text{SnCH}_2\text{N}$ 	$n\text{-BuLi}$	Hexane	$\text{LiCH}_2\text{N}$ 	71

<sup>a</sup>  $\text{R} = \text{C}_6\text{H}_{13}$  <sup>75,77</sup>,  $\text{C}_6\text{H}_{11}$  <sup>75</sup>,  $\text{C}_5\text{H}_{11}$  <sup>77</sup>,  $\text{Me}$  <sup>77</sup>,  $\text{H}$  <sup>75</sup>,  $\text{Ph}$  <sup>77</sup>,  $m\text{-}$  or  $p\text{-MeOC}_6\text{H}_4$  <sup>77</sup>, 3-furyl <sup>75</sup>.

The stereospecific nature of the exchange is also reflected in reactions of separated diastereomers<sup>76</sup>:

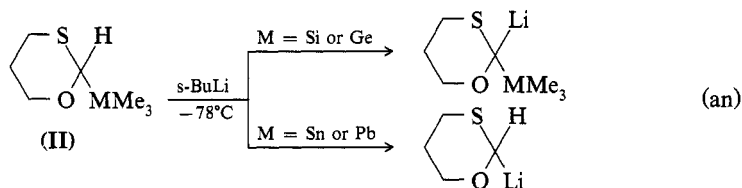


Treatment of  $n\text{-Bu}_3\text{SnCH}_2\text{OH}$  with 2 equiv  $n\text{-BuLi}$  provides a pentane-soluble reagent that hydroxymethylates electrophilic centers in moderate yields. The intermediate species is not the free  $\text{LiCH}_2\text{OLi}$ , but the more complex<sup>78</sup>:

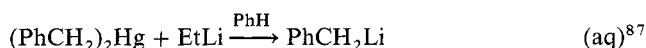
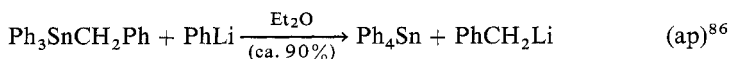
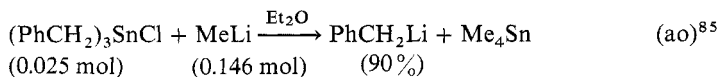


Although the HO group is remote from Sn in  $n\text{-Bu}_3\text{Sn(CH}_2\text{)}_3\text{OH}$ , it enhances the reactivity of the  $\text{Sn-C}$  bond because  $n\text{-Bu}_3\text{Sn(CH}_2\text{)}_3\text{OH}$  undergoes transmetalation with  $n\text{-BuLi}$  to provide<sup>78</sup>  $\text{Li(CH}_2\text{)}_3\text{OLi}$ .

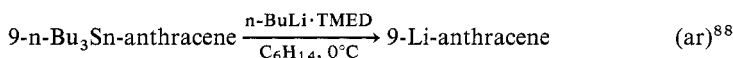
Reactions of (III) with *s*-BuLi show differences between the Si and Ge analogues on one hand, and the Sn and Pb compounds on the other<sup>84</sup>:



(vi) **Benzyllithiums.** Benzyllithium is prepared in several ways:

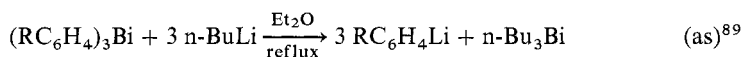


Naphthyl- and anthracenyl derivatives are prepared by transmetallations, e.g.:

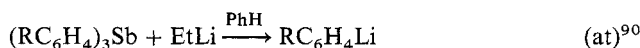


(vii) **Aryllithiums.** Transmetallations provide:

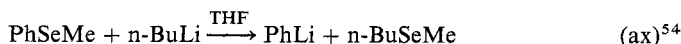
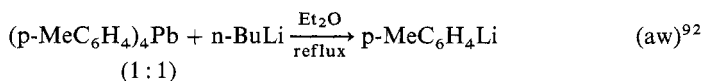
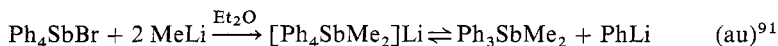
(a) Simple aryllithiums:



where R = *p*-Me, *p*-Cl, *o*-EtO;

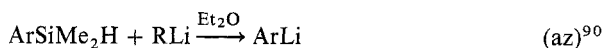
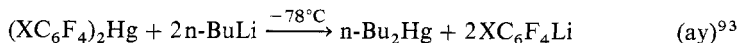


where R = *p*-Me, *o*-Me, *m*-Me, *p*-Br, *p*-Cl, *p*-Ph;



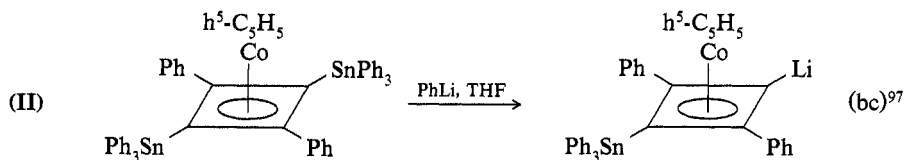
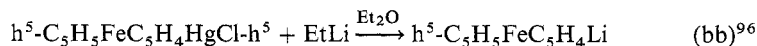
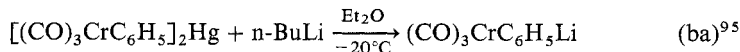


## b. Haloaryllithiums:



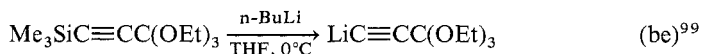
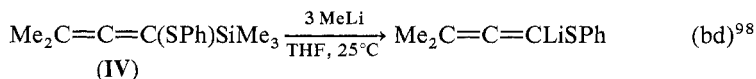
where Ar = C<sub>6</sub>F<sub>5</sub> (R = n-Bu); C<sub>6</sub>Cl<sub>5</sub> (R = Me); p-C<sub>5</sub>Cl<sub>4</sub>N (R = n-Bu)

## c. Lithiated transition-metal complexes:



Only one SnPh<sub>3</sub> group is replaced.

(viii) Other Organolithiums. Allenyl- and alkynyllithiums are formed by transmetallations:



In contrast to Eq. (bd), (IV) reacts with t-BuLi to give Me<sub>2</sub>C=C=CLiSiMe<sub>3</sub>.

(J. L. WARDELL)

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#### 5.5.2.3.2. by Proton–Metal Exchange with Acidic C—H Bonds.<sup>1–5</sup>

Lithiation, replacement of hydrogen in an organic compound by Li, can be achieved using R'Li or R'<sub>2</sub>NLi:



These are equilibria whose positions depend on the relative acidities of the proton sources. The more acidic compound provides the greater amount of organolithium and so the greater the difference in the acidity, the larger the equilibrium constant. However, kinetic acidities must be considered as well as thermodynamic ( $\text{pK}_\text{a}$  values); e.g., PhH ( $\text{pK}_\text{a}$  37) is not metallated by alkylolithiums [ $\text{pK}_\text{a}$  of alkanes > 40 in tetrahydrofuran (THF)], despite large difference in  $\text{pK}_\text{a}$  values. The more reactive RLi·TMED (tetramethylethylenediamine) complexes, however, provide PhLi. The equilibrium can be driven to the product side by removing the product hydrocarbon or precipitating the RLi.

Knowledge of  $\text{pK}_\text{a}$  values, however, is useful, and Table 1 lists these for important hydrocarbons<sup>6,7</sup>.

The most frequently used carbanionic lithiating agents, RLi, are MeLi, n-BuLi, s-BuLi and t-BuLi. The RLi compounds are aggregates, the degree of aggregation depending on the bulk of R, concentration and solvent.<sup>4,5</sup> They are electron-deficient compounds, i.e., electron-pair acceptor acids, which on coordination with electron-pair donor bases, in particular ethers and amines, depolymerize to smaller units; e.g., addition of TMED to hexameric n-BuLi in hydrocarbons forms the coordinatively saturated, monomeric n-BuLi·TMED. An exception is MeLi, for which the tetramer persists even in THF or on addition of TMED.

44      5.5. Formation of Bonds between Elements of Groups IVB and IA  
           5.5.2. Carbon–Lithium Bonds  
           5.5.2.3. from Other Organolithiums

74. U. Schöllkopf, in *Methoden der Organischen Chemie (Houben-Weyl)*, Band XIII/1, *Metallorganische Verbindungen Li, Na, K, Rb, Cs, Cu, Ag, Au*, Georg Thieme Verlag, Stuttgart, 1970, p. 87.
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**5.5.2.3.2. by Proton–Metal Exchange with Acidic C—H Bonds.**<sup>1–5</sup>

Lithiation, replacement of hydrogen in an organic compound by Li, can be achieved using R'Li or R'<sub>2</sub>NLi:



These are equilibria whose positions depend on the relative acidities of the proton sources. The more acidic compound provides the greater amount of organolithium and so the greater the difference in the acidity, the larger the equilibrium constant. However, kinetic acidities must be considered as well as thermodynamic (pK<sub>a</sub> values); e.g., PhH (pK<sub>a</sub> 37) is not metallated by alkyllithiums [pK<sub>a</sub> of alkanes > 40 in tetrahydrofuran (THF)], despite large difference in pK<sub>a</sub> values. The more reactive RLi·TMED (tetramethylethylenediamine) complexes, however, provide PhLi. The equilibrium can be driven to the product side by removing the product hydrocarbon or precipitating the RLi.

Knowledge of pK<sub>a</sub> values, however, is useful, and Table 1 lists these for important hydrocarbons<sup>6,7</sup>.

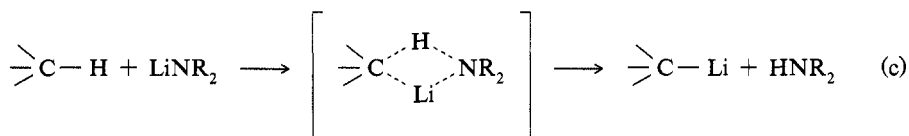
The most frequently used carbanionic lithiating agents, RLi, are MeLi, n-BuLi, s-BuLi and t-BuLi. The RLi compounds are aggregates, the degree of aggregation depending on the bulk of R, concentration and solvent.<sup>4,5</sup> They are electron-deficient compounds, i.e., electron-pair acceptor acids, which on coordination with electron-pair donor bases, in particular ethers and amines, depolymerize to smaller units; e.g., addition of TMED to hexameric n-BuLi in hydrocarbons forms the coordinatively saturated, monomeric n-BuLi·TMED. An exception is MeLi, for which the tetramer persists even in THF or on addition of TMED.

TABLE 1. HYDROCARBON  $pK_a$  SCALE

Compound	$pK_a$
Fluoradene	11
Cyclopentadiene	15
9-Phenylfluorene	18.5
Indene	18.5
Phenylacetylene	18.5
Fluorene	22.9
Acetylene	25
1,3,3-Triphenylpropene	26.5
Triphenylmethane	32.5
Toluene ( $\alpha$ -position)	35
Propene ( $\alpha$ -position)	35.5
Cycloheptatriene	36
Ethylene	36.5
Benzene	37
Cumene ( $\alpha$ -position)	37
Triptycene ( $\alpha$ -position)	38
Cyclopropane	39
Methane	40
Ethane	42
Cyclobutane	43
Neopentane	44
Propane ( $s$ -position)	44
Cyclopentane	44
Cyclohexane	45

Kinetically, these reagents become more basic as aggregate size diminishes; more reactive species are obtained in ethers, e.g., in  $\text{Et}_2\text{O}$  or THF, than in hydrocarbons or on addition of a donor molecule, e.g., TMED<sup>8</sup>, triethylenediamine (DABCO), hexamethylphosphorictriamide (HMPA) or dimethylsulfoxide (DMSO). Kinetic studies of metallations by  $\text{RLi}$  in hydrocarbons or ethers reveal fractional orders in  $\text{RLi}$ . These arise from dissociation of the larger oligomers, (tetramers and hexamers) to smaller and more reactive species (monomers and dimers) in pre-rate-determining steps. Increasing basicity of the solvent should also help to stabilize the transition state.

The most frequently used Li dialkylamides are N-Li tetramethylpiperidine ( $\text{Li}\cdot\text{TMP}$ ) and Li diisopropylamide,  $\text{LiN}(\text{Pr-}i)_2$ . The noncarbanionic,  $\text{LiNR}_2$ , are poor electron-pair acceptor acids. They are also poor nucleophiles and so can be used more widely and safely than can  $\text{RLi}$  agents, e.g., with carbon acids having reactive hetero-substituted groups. Lithium dialkylamides,  $\text{LiNR}_2$ , have reduced thermodynamic basicities relative to  $\text{RLi}$ , with  $pK_a$ s of  $\text{HNR}_2$  ca. 30. However, they are more effective metallating agents (i.e., show an increased kinetic basicity), a consequence of the use of the nitrogen lone pair in the transition state:



For lithiations by RLi, the mechanism is based on a simple acid–base interaction with substitution at the most acidic site; for hetero-substituted compounds an alternative mechanism is one based on prior coordination of RLi to the heteroatom<sup>9</sup> which leads to lithiation of neighboring sites, i.e., ortho, alpha or beta to the heteroatom.

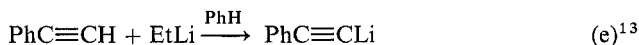
(i) Lithiation of Hydrocarbons. As deduced from the  $pK_a$  values in Table 1, alkynyl, benzylic and allylic hydrogens are more acidic than alkyl hydrogens ( $\Delta pK_a > 9$ ). Reactions of hydrocarbons containing such hydrogens occur with simple alkylolithiums and go to completion.

a. Alkynyl and Propargylic Lithiums. Acetylene is dimetallated<sup>10</sup>, even by PhLi:

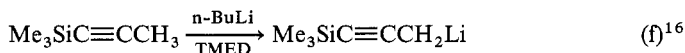


Monolithioacetylene,  $\text{LiC}\equiv\text{CH}$ , is produced by the disproportionation<sup>11</sup> of  $\text{LiC}\equiv\text{CLi}$  and  $\text{HC}\equiv\text{CH}$  in liq  $\text{NH}_3$  or from<sup>12</sup>  $\text{HC}\equiv\text{CH}$  with  $n\text{-BuLi}$  in THF at  $-78^\circ\text{C}$ .

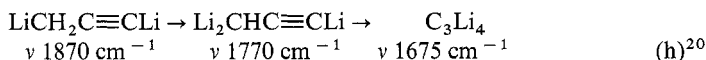
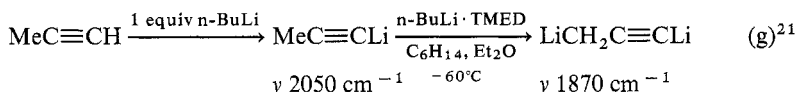
Terminal alkynes,  $\text{RC}\equiv\text{CH}$  also react, e.g.<sup>13–15</sup>:



Propargylic hydrogens are sufficiently acidic to be replaced by Li using alkylolithiums, e.g.<sup>16–19</sup>:

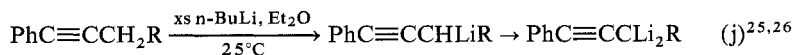
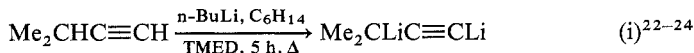


Replacement of propargylic as well as alkynyl hydrogen in the same compound can arise to give di- and polyolithio products<sup>20</sup>; e.g.,  $\text{MeC}\equiv\text{CH}$  with  $n\text{-BuLi}$  (1 equiv) provides  $\text{MeC}\equiv\text{CLi}$ , and with xs  $n\text{-BuLi}$  successive replacements of hydrogens occur to give  $\text{C}_3\text{Li}_4$  finally. The structures of these anionic compounds are deduced from IR data:



The terminal alkyne 1-butyne is lithiated by  $n\text{-BuLi}$  or  $t\text{-BuLi}$  (3 equiv) to  $\text{MeC}_3\text{Li}_3$ ; the same  $\text{MeC}_3\text{Li}_3$  product can be obtained from the internal alkyne if the more powerful metallating agent,  $n\text{-BuLi} \cdot \text{TMED}$  (3 equiv), is used<sup>22–24</sup>.

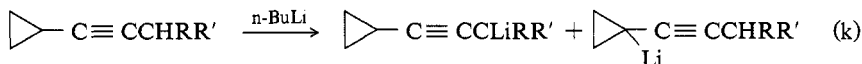
Dilithiated products can be obtained, e.g.:



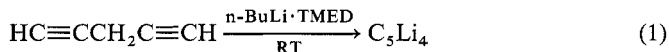
where  $\text{R} = \text{H}$  or  $\text{Me}$ .

Reaction of  $n\text{-BuLi} \cdot \text{TMED}$  with  $\text{PhC}\equiv\text{CMe}$  leads to lithiation at the ring as well as propargylic sites to give<sup>22–24</sup> o- and p- $\text{LiC}_6\text{H}_4\text{C}\equiv\text{CCLi}_3$ ; more forcing conditions lead to even further lithiation.

Competition between metallation of different propargylic centers is shown in:

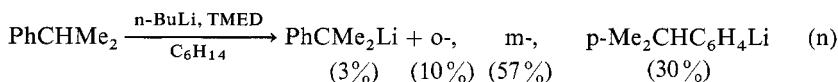
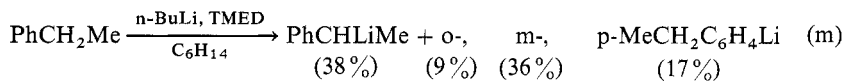


Monometallation<sup>27</sup> occurs at the propargylic group for R, R' = H in the cyclopropyl ring for R, R' = Me, and at either site for R = H, R' = Me. The diyne, HC≡CCH<sub>2</sub>C≡CH, can be perlithiated<sup>24</sup> to C<sub>5</sub>Li<sub>4</sub>; under similar conditions MeC≡CC≡CMe provides MeC<sub>5</sub>Li<sub>3</sub>:



b. Benzylic Lithiums and Related Compounds. Toluene is metallated<sup>28</sup> (and even polyolithiated)<sup>20</sup> at a reasonable rate by n-BuLi·TMED, but not by n-BuLi in THF. Compounds with more acidic benzylic hydrogens, e.g., p-PhC<sub>6</sub>H<sub>4</sub>Me, (p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub>, Ph<sub>2</sub>CH<sub>2</sub> and Ph<sub>3</sub>CH, are metallated by n-BuLi in THF at benzylic positions, the reactivity increasing in the sequence given<sup>29</sup>.

The initial products<sup>28,30</sup> from PhMe with n-BuLi·TMED include ≤ 10% ring-metallated ones as well as PhCH<sub>2</sub>Li. These ring-metallated products slowly rearrange to the thermodynamically more stable product, PhCH<sub>2</sub>Li·TMED, on standing, on addition of xs TMED, or preferably on heating<sup>28</sup>. Lithiations<sup>30</sup> of PhCH<sub>2</sub>Me and PhCHMe<sub>2</sub> using n-BuLi·TMED provide mixtures containing greater proportions of ring-metallated species. These ring-metallated products do not rearrange to benzylic anionic products:

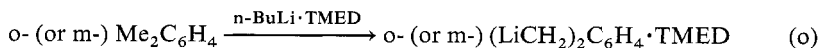


The reactivity<sup>30</sup> of the benzylic sites is in the sequence PhMe:PhEt:PhPr-i = 6:1:0.1 and shows the deactivating effect of Me groups at the carbanionic center.

Benzocyclobutene is also metallated by n-BuLi·TMED in Et<sub>2</sub>O, both in the aryl ring and in the cyclobutene ring, i.e., at the benzylic sites<sup>31</sup>.

Different lithiation products of MeCH(C<sub>6</sub>H<sub>4</sub>Me-p)<sub>2</sub> are obtained with different lithiating agents; e.g., t-BuLi in THF produces MeCH(C<sub>6</sub>H<sub>4</sub>Me-p)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Li-p (I), the kinetic product, and MeCH(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Li-p)<sub>2</sub>, whereas PhCH<sub>2</sub>Li gives the thermodynamic product, LiCMe(C<sub>6</sub>H<sub>4</sub>Me-p)<sub>2</sub> (II). Compound I rearranges<sup>32</sup> to II.

The reactivity of xylenes in metallations using n-BuLi·TMED is m- > o- > p-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. Both Me groups of o- or m-xylene can be lithiated:

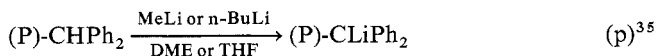


Additional polyolithated products from m-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub> are m-Li<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>Me and m-Li<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Li. The products from p-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub> are p-LiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me and, under forcing conditions<sup>33</sup>, p-Li<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>Me, but not p-(LiCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. The ease of dimetallation arises from charge densities; the negative charge on a benzylic anion is delocalized into

the ring in the order:  $m- < o- < p-$ . Another explanation for the sequence of dimetallation ( $m- < o-$  and  $p-$ ) is that the second metallation occurs to give the new negative charges on the same carbon atoms as did the first. The easier formation of  $o-(LiCH_2)_2C_6H_4$  compared to the para isomer arises from the lone-pair attractions between the adjacent benzylic sites of the ortho isomer. Another consideration is that Li can bridge the benzylic and the ortho sites during metallation (as happens in solid benzyl lithium), and so the greater the negative charge on the ortho site, the stronger is this interaction and the more facile the substitution. No ring metallation results in these reactions.

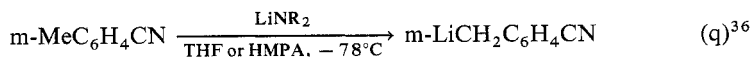
The tri- and tetramethylbenzenes behave<sup>33,34</sup> like the xylenes; e.g., 1,3,5- $Me_3C_6H_3$  and  $n-BuLi \cdot TMED$  in hexane provide mono-, di- and trilithiated mesitylenes. The major product is 1,3,5- $(LiCH_2)_3C_6H_3$  with dilithiation occurring partially on the same methyl group, but preferentially at different methyls. No bis-1,4- $LiCH_2$  compound is obtained from 1,4-dimethyl aromatics, such as 1,2,4- $Me_3C_6H_3$  or 1,2,4,5- $Me_4C_6H_2$ .

A polymeric benzylic Li is produced by lithiation:

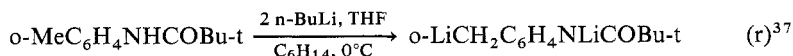


where (P) = polystyryl residue and DME is 1,2-dimethoxyethane.

Substituted toluenes,  $XC_6H_4Me$ , can be metallated using  $RLi$  or  $LiNR_2$ , at the benzylic positions, e.g.:

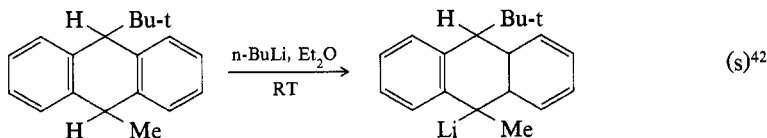


where  $R = Me$  or  $i-Pr$ ;

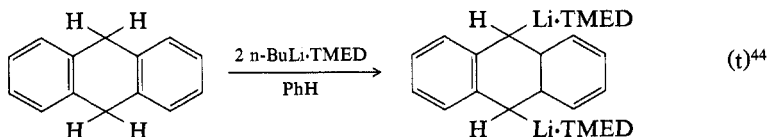


Other  $XC_6H_4Me$  lithiated similarly include those with  $X = o-HO_2C$ <sup>38</sup>,  $o-CN$ <sup>39</sup>,  $o-Me_2N$ <sup>40</sup> and  $o-RNHSO_2$ <sup>41</sup>. These  $o-X$  groups aid metallation at the benzylic site by coordinating with  $RLi$  (i.e., directed lithiations).

9,10-Dihydroanthracenes can be mono-<sup>42,43</sup> or dimetallated<sup>44,45</sup> at the 9- or 10-positions using  $RLi$  under a variety of conditions, e.g.:



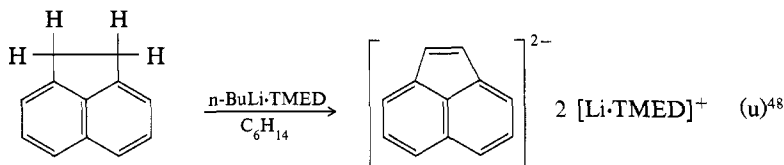
(III)



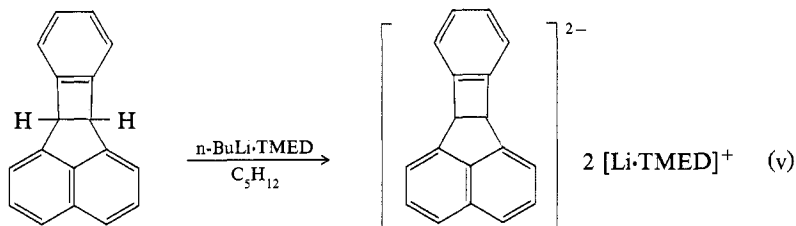
Relative reactivities<sup>42</sup> of cis and trans (III) are 20 : 1.



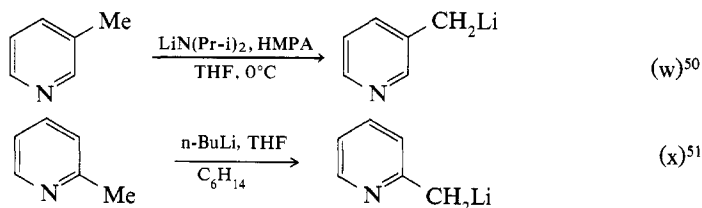
Methylnaphthalenes are metallated at the benzylic position with a 2-Me more reactive than a 1-Me, e.g., as found in 1,2,3,4-tetramethylnaphthalene<sup>46</sup>. 1,8-Dimethylnaphthalene is only monometallated<sup>47</sup> by xs *n*-BuLi at a methyl group, although the related compound, acenaphthylene, is dimetallated<sup>48</sup>:



6b,10b-Dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene<sup>49</sup> reacts similarly with *n*-BuLi-TMED:

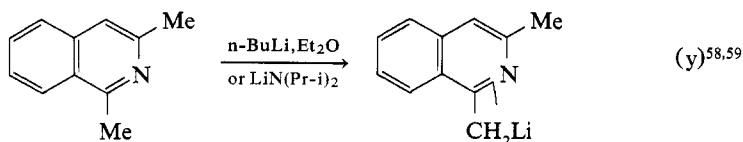


Methyl heteroaromatics are lithiated readily. Lithiation occurs at the methyl groups in methylpyridines<sup>50–56</sup>, quinolines<sup>55–57</sup> and isoquinolines<sup>58,59</sup>, e.g.:



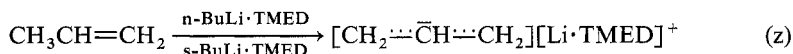
For 2,4-dimethylpyridines or -quinolines, the group metallated depends on whether kinetic or thermodynamic control operates: the kinetic products are the 3-LiCH<sub>2</sub> derivatives (e.g., as obtained using *n*-BuLi in Et<sub>2</sub>O), whereas the thermodynamic products are the 4-LiCH<sub>2</sub> derivatives<sup>56</sup> (e.g., as produced from  $LiNR_2$  in THF). Conversion of kinetic to thermodynamic products occurs predictably, e.g., on standing and on increasing the polarity of the solvent.

1,3-Dimethylisoquinoline is lithiated at the 1-Me position irrespective of the lithiating agent or conditions:

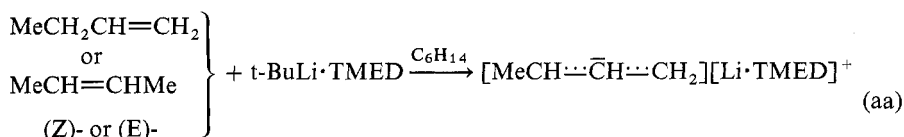


Lithiation of the methyl derivatives of such five-membered heteroaromatics as pyrrole<sup>60</sup>, thiophene<sup>61,62</sup>, 1,3-thiazole<sup>60,63,64</sup>, 1,3-oxazole<sup>65,66</sup>, isoxazole<sup>67</sup>, 1,3,4-thiadiazole<sup>63</sup>, 1,3,4-oxadiazole<sup>63</sup> and imidazole<sup>68</sup> also occurs. For the sulfur heterocyclics, ring metallations and ring opening after lithiation are complications.

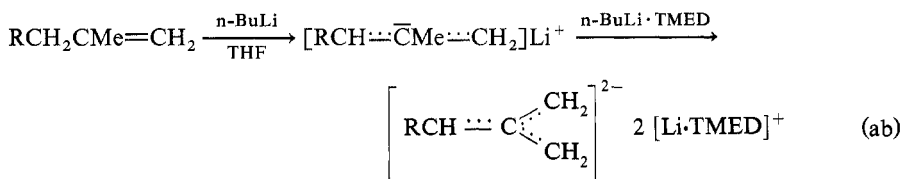
c. Allyllithiums and Related Compounds. Lithiation of propene ( $pK_a = 35.5$ ) to allyllithium occurs using *n*-BuLi in THF<sup>69</sup>, *n*-BuLi·TMED<sup>28,69</sup>, or *s*-BuLi·TMED<sup>28</sup>. The *s*-BuLi is more effective than the *n*-BuLi:



*t*-Butyllithium is used also. Crotyllithium is prepared from butenes<sup>28,70</sup> using *t*-BuLi·TMED:

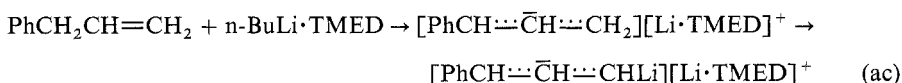


Isobutene<sup>71,72</sup> and methylallylbenzenes<sup>71</sup> are dimetallated by *n*-BuLi·TMED; in contrast, use of *n*-BuLi in THF leads only to monolithiation:

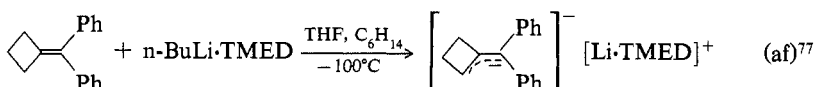
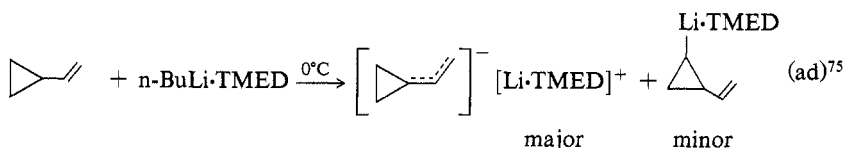


where R = H or Ph.

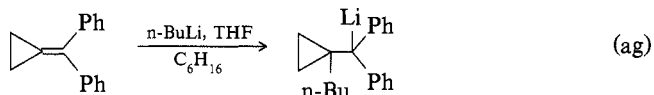
Propene<sup>73</sup>, 1-butene<sup>74</sup>, 2-butene<sup>74</sup>, and  $\text{PhCH}_2\text{CH}=\text{CH}_2$ <sup>73</sup> also are dimetallated by *n*-BuLi·TMED, but more forcing conditions are required than for  $\text{RCH}_2\text{CMe}=\text{CH}_2$  (R = H or Ph), e.g.<sup>73</sup>:



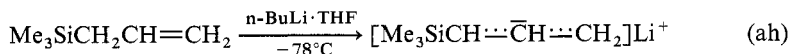
Other substituted allyllithiums may be prepared similarly:



In contrast to metallation of the cyclobutyl derivative in Eq. (af), the reaction of the cyclopropyl analogue with *n*-BuLi leads to addition:

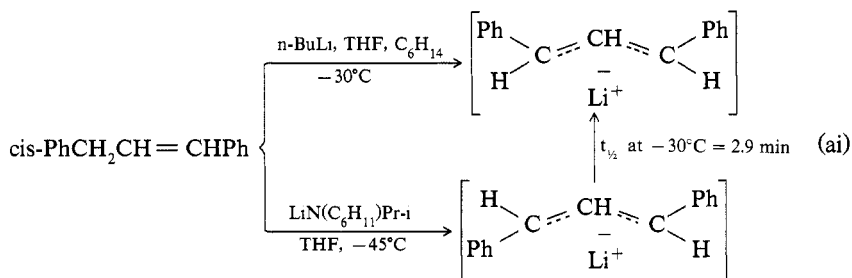


Metallation of allylsilanes also occurs, e.g.<sup>78</sup>:



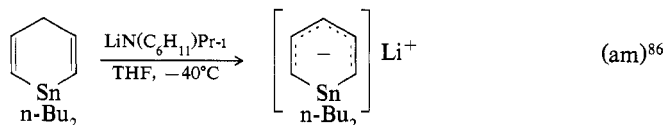
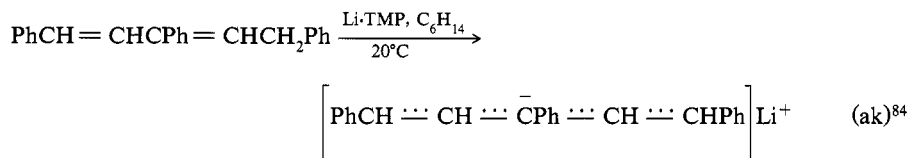
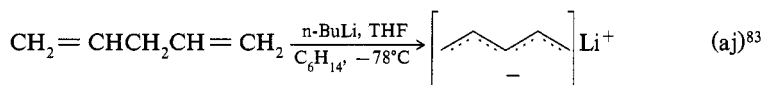
Whereas allylic metallation of  $\text{Ph}_2\text{Si}(\text{CH}=\text{CH}_2)\text{CH}_2\text{CH}=\text{CH}_2$  results from MeLi·TMED, addition to the vinyl group occurs using *n*-BuLi·TMED to form<sup>79</sup>  $\text{Ph}_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)\text{CHLiCH}_2\text{Bu-n}$ .

An increase in conjugation leads to more facile metallation<sup>80–82</sup>, as shown by  $\text{PhCH}_2\text{CR}=\text{CH}_2$  ( $\text{R} = \text{Me}$  or  $\text{H}$ ) and by  $\text{PhCH}_2\text{CH}=\text{CHPh}$ :

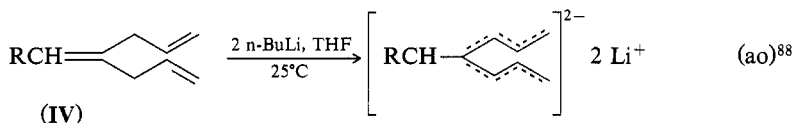
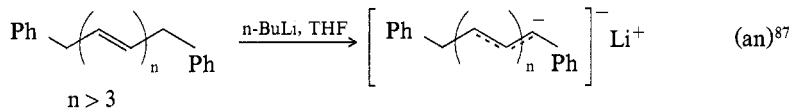


Either  $\text{LiNR}_2$  or  $\text{RLi}$  may be used. At  $-45^\circ\text{C}$  using  $\text{LiNR}_2$ , the (E,Z) isomer is produced; this is isomerized to the (E,E) isomer, produced directly from *n*-BuLi at  $-30^\circ\text{C}$ .

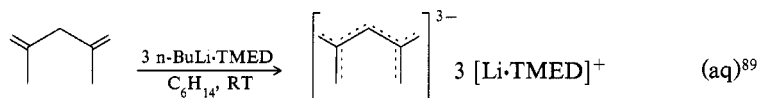
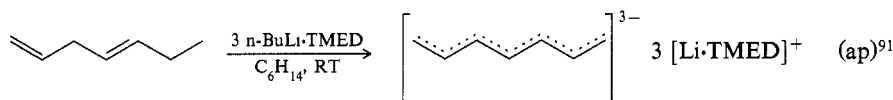
Pentadienyllithiums are prepared similarly, e.g.:



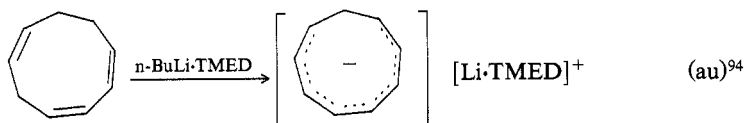
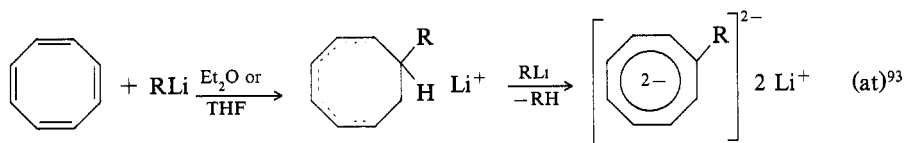
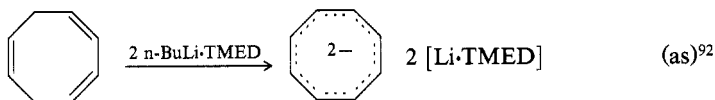
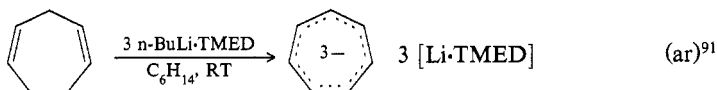
More highly conjugated anions can be prepared, e.g.:

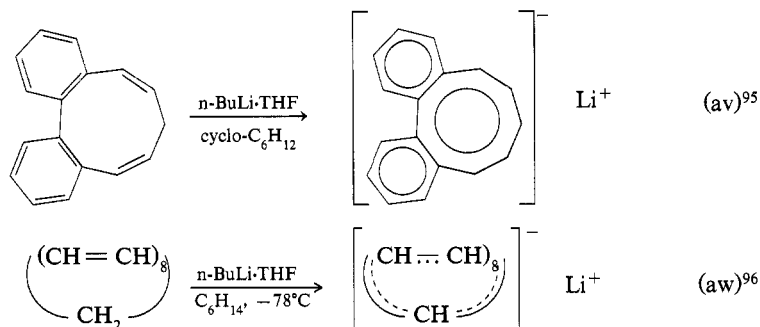


where R = H or Ph. The monoanion of (IV) is metallated to the dianion and cannot be isolated<sup>88</sup>, even in Et<sub>2</sub>O. Dilithiation of the dienes CH<sub>2</sub>=CHCH<sub>2</sub>CH=CH<sub>2</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>CH=CHMe, CH<sub>2</sub>=CMeCH<sub>2</sub>CMe=CH<sub>2</sub> or CH<sub>2</sub>=CMeCH<sub>2</sub>CH=CH<sub>2</sub> occurs<sup>74,89,90</sup> slowly with n-BuLi·TMED; crystalline TMED adducts are obtained<sup>89,90</sup>. Trianionic compounds may be obtained also<sup>89,91</sup>:

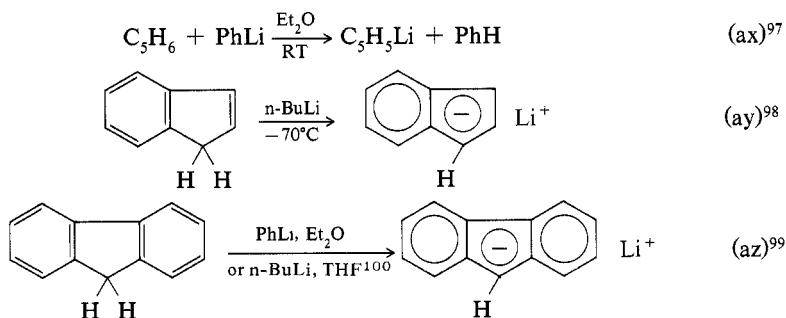


Cyclic delocalized mono-, di- and trianionic compounds also are prepared:



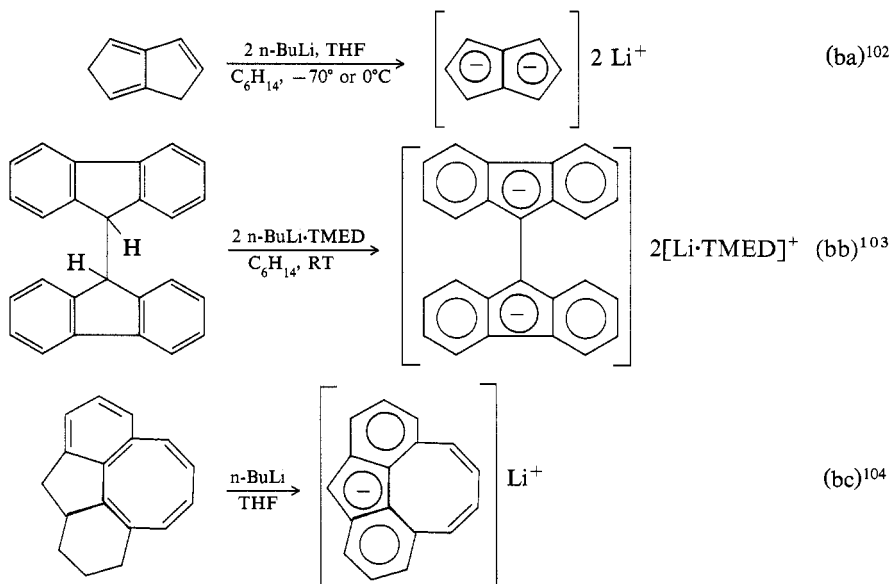


Cyclopentadienyllithiums. Cyclopentadiene, indene and fluorene ( $\text{pK}_a = 15, 18.5, 22.9$ , respectively) are metallated by alkylolithium and even by  $\text{PhLi}$ , e.g.:



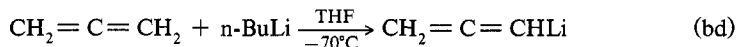
Polyolithiation of indene and fluorene occurs using  $\text{n-BuLi} \cdot \text{TMED}$  at  $70^\circ\text{C}$ ; compounds with up to six and nine Li are obtained from indene and fluorene, respectively<sup>101</sup>.

More complex derivatives also react, e.g.:



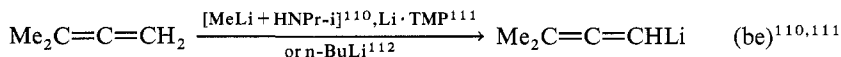
Other related metallations by *n*-BuLi include those of 7bH-indeno[1,2,3jk]fluorene<sup>105</sup>, 4,11-dihydrodicyclopenta[def,pqr]tetraphenylene<sup>106</sup> and syn- or anti-[2.2](2,7)fluorene-phane<sup>107</sup>.

e. Allenyllithiums. Allene is metallated<sup>108,109</sup> by *n*-BuLi in THF at <0°C:

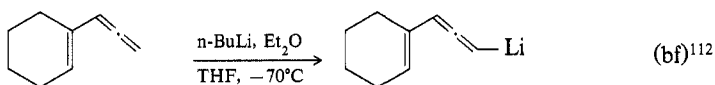


Dilithiation of allene leads to the acetylene<sup>108</sup>  $\text{LiCH}_2\text{C}\equiv\text{CLi}$ .

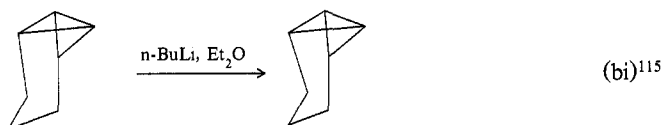
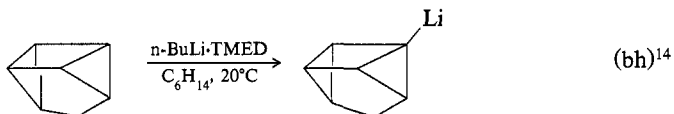
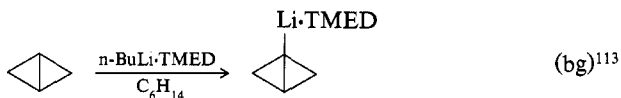
Alkyl-substituted allenes also react, e.g.:



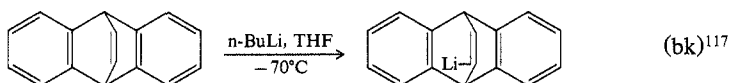
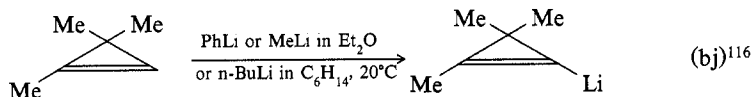
as do alkenyl allenes, e.g.:



f. Cyclopropyllithiums. The increased acidity of bridgehead hydrogens in cyclopropyl rings in bi- and polycyclic compounds renders these compounds reactive toward *n*-BuLi, e.g.:



g. Alkenyllithiums. Unless they are carrying hetero-substituted groups or are severely strained, alkenes do not take part in lithiation at the double bond, e.g.:



h. Unsubstituted Aryllithiums. Although the difference in  $\text{pK}_a$  values of PhH and *n*-BuH is ca. 5, PhH is not metallated by *n*-BuLi in  $\text{C}_6\text{H}_{14}$ . Benzene is poorly metallated by *n*-BuLi in  $\text{Et}_2\text{O}$ . Increased reactivity is found,<sup>4,28</sup> with *n*-BuLi in THF and especially with *n*-BuLi·DABCO or *n*-BuLi·TMED.

Polynuclear aromatics such as PhPh, naphthalene, or anthracene are metallated more readily or even polymetallated<sup>101</sup>.

(ii) Lithiation of Hetero-Substituted Hydrocarbons. Hetero-substituted functional groups can enhance the acidity (or reactivity) of  $\alpha$  (or  $\beta$ ) protons in alkyl and alkenyl compounds and/or ortho protons in aromatic compounds and hence make lithiations<sup>4,9,118-121</sup> easier to effect using either RLi or LiNR<sub>2</sub>. Low T and the less nucleophilic LiNR<sub>2</sub> as lithiating agent frequently are necessary to avoid reactions involving the functional group. Such side reactions include additions, couplings and eliminations.

(iii) Lithiation of  $\alpha$ -Hetero-Substituted Alkanes. The heteroatom may be N, P, As, Sb, O, S, Se, Te, F, Cl or Br in a variety of groups (see Tables 3-12). In addition,  $\alpha$ -R<sub>2</sub>B or -R<sub>3</sub>Si stabilizes carbanionic centers.<sup>122,123</sup> Combinations of the same or different groups increase acidity and so make lithiation even easier.

Not all  $\alpha$ -hetero substituents enhance acidity; e.g., the pK<sub>a</sub>s of PhSO<sub>2</sub>Me and PhSO<sub>2</sub>CH<sub>2</sub>OMe are 29 and 30.7, respectively (see Table 2). This is also indicated by base-catalyzed hydrogen exchanges being retarded when  $\alpha$ -RO groups<sup>124</sup> are present.

Thermodynamic acidities of substituted alkanes are known in DMSO<sup>125-128</sup>, cyclohexylamine<sup>129</sup> and in the gas phase<sup>130</sup>.

Selected pK<sub>a</sub> values are assembled in Table 2.

TABLE 2. pK<sub>a</sub> VALUES FOR  
HETEROSUBSTITUTED ALKANES<sup>a</sup>

Compound	pK <sub>a</sub>
CH <sub>4</sub>	40
MeSO <sub>2</sub> Ph	29
MeSO <sub>2</sub> CF <sub>3</sub>	18.8
MeNO <sub>2</sub>	17.2
CH <sub>2</sub> (SO <sub>2</sub> Ph) <sub>2</sub>	12.2
CH <sub>2</sub> (SPh) <sub>2</sub>	30.8
CH <sub>2</sub> (SePh) <sub>2</sub>	35.0
CH(SPh) <sub>3</sub>	22.8
PhSO <sub>2</sub> CH <sub>2</sub> OMe	30.7
PhSO <sub>2</sub> CH <sub>2</sub> OPh	27.9
PhSO <sub>2</sub> CH <sub>2</sub> SPh	20.3
PhSO <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>	20.2
PhSO <sub>2</sub> CH <sub>2</sub> Ph	23.4
1,3-Dithiane	31.2 <sup>129</sup>
Me <sub>2</sub> SO	35.1
Me <sub>2</sub> SO <sub>2</sub>	31.1
MeCH <sub>2</sub> CN	32.5
MeCH <sub>2</sub> COPh	24.4
MeCH <sub>2</sub> SO <sub>2</sub> Ph	31
MeCH <sub>2</sub> SO <sub>2</sub> CF <sub>3</sub>	20.4
MeCH <sub>2</sub> NO <sub>2</sub>	16.7
PhOCH <sub>2</sub> COPh	21.1
PhSCH <sub>2</sub> COPh	17.1
PhSeCH <sub>2</sub> COPh	18.6
PhSCH <sub>2</sub> Ph	30.8
PhOSO <sub>2</sub> CH <sub>2</sub> Ph	21.7 <sup>131</sup>

<sup>a</sup> Refs 125-128 unless otherwise stated

Polyhalo substitution increases acidity<sup>132</sup>; e.g.,  $pK_a$  values for  $CHX_3$  in DMSO are<sup>133</sup> 28–31, 15.5, 13.7, 13.7 or 11 for  $X = F, Cl, Br, I$  or  $CF_3$ , compared to  $pK_a = 40$  for  $CH_4$ .

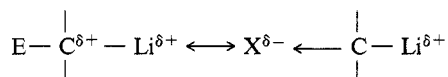
In addition to these thermodynamic values, kinetic acidities also may be obtained. The relative rates of deuterium–hydrogen exchange (at the Me group) using  $KNH_2$  in  $NH_3$  are<sup>134</sup>  $PhNMe_2$  (1):  $PhPMe_2$  ( $3 \times 10^4$ ):  $PhOMe$  ( $4 \times 10$ ):  $PhSMe$  ( $2 \times 10^8$ ):  $PhSeMe$  ( $2 \times 10^7$ ) and  $PhSMe$  ( $2 \times 10^8$ ):  $PhSEt$  ( $2 \times 10^6$ ):  $PhSPri$  ( $2 \times 10^4$ ):  $MeSMe$  ( $6 \times 10^2$ ) for reaction at the CH bonds  $\alpha$  to sulfur.

The relative rates of lithiation<sup>135</sup> of  $m-CF_3C_6H_4SMe$  and  $m-CF_3C_6H_4SeMe$  by  $LiN(Pr-i)_2$  in THF–PhMe at  $-56^\circ C$  are 4:1.

Orthometallation of  $PhXCHR'R'$  (to give  $o-LiC_6H_4XCHRR'$ ) may compete and may even be the sole reaction for certain X (e.g., O, NMe) and for certain combinations of X, R and R' groups; e.g., ring metallation of  $m-CF_3C_6H_4SCH_2Me$  occurs using  $Li \cdot TMP$ . The formation of  $2-Li-5-CF_3C_6H_4SCH_2CH_3$ , instead of the side-chain metallation product  $m-CF_3C_6H_4SCHLiMe$ , is a consequence of the deactivating effect of the Me group on the  $\alpha$  site<sup>135</sup>.

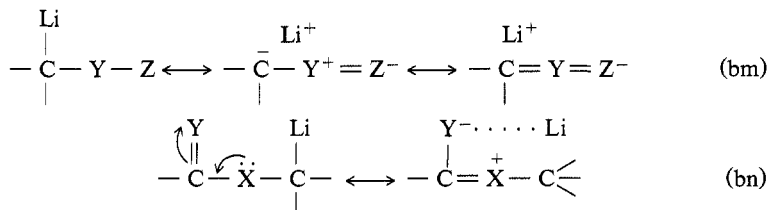
The stability of hetero-substituted carbanions depends on:

1. The inductive effects (electron-withdrawing effects) of the hetero-substituted groups:



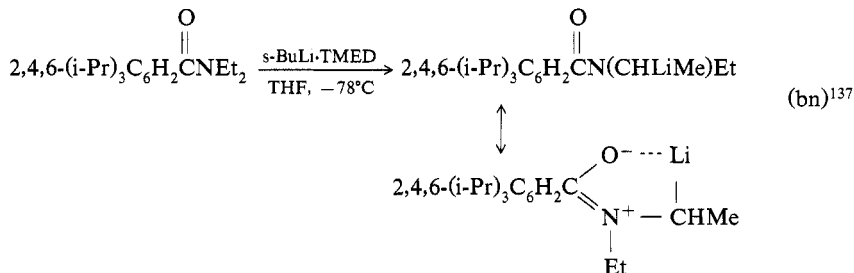
where E = electronegative groups, e.g., Ph, X, or  $CX_3$  (X = halogen).

2. Charge–dipole interactions<sup>136</sup>:



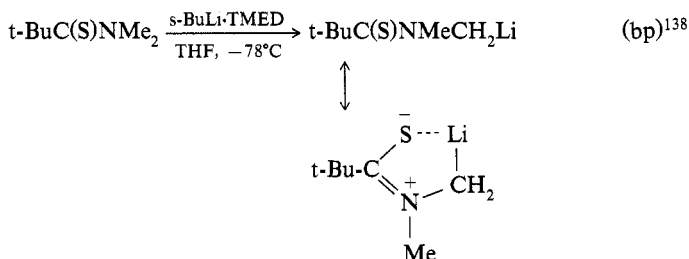
where X = O, S or NR; Y = O or S. Some examples are:

From amides, e.g.:

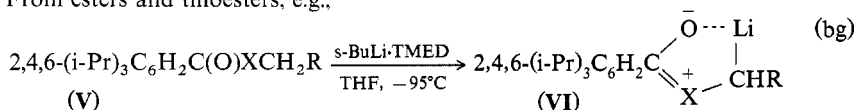




From thioamides, e.g.:

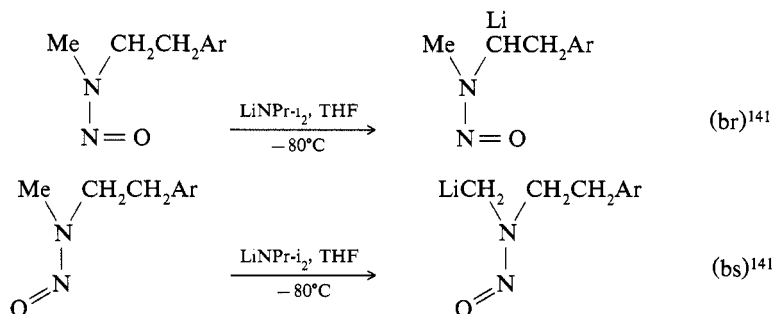


From esters and thioesters, e.g.,



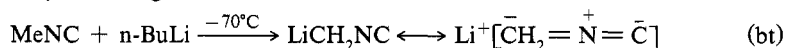
where if  $\text{X} = \text{O}$ ,  $\text{R} = \text{H}$  <sup>139</sup> and if  $\text{X} = \text{S}$ ,  $\text{R} = \text{Me}$  <sup>137</sup>. The stability of VI ( $\text{X} = \text{S}$ ,  $\text{R} = \text{H}$ ) is indicated <sup>137</sup> from the metallation of V ( $\text{X} = \text{S}$ ,  $\text{R} = \text{H}$ ) by the stabilized carbanionic species,  $\text{CH}_3\text{SCH}_2\text{Li}$  in THF at  $-78^\circ\text{C}$ .

From nitrosamines, e.g. <sup>140,141</sup>:

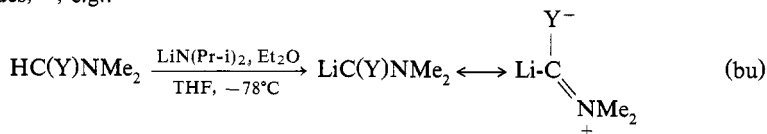


Lithiation occurs at the carbon syn to the nitroso oxygen.

From isocyanides, e.g. <sup>142</sup>:

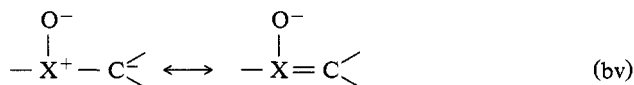


Other dipole-stabilized carbanions are obtained from succinimides <sup>143</sup>, amine oxides <sup>144</sup>, nitroalkanes <sup>145</sup>, thioimides <sup>146</sup>, dithiocarbonates <sup>147</sup>, formamides <sup>148</sup> and thioformamides, <sup>149</sup>, e.g.:



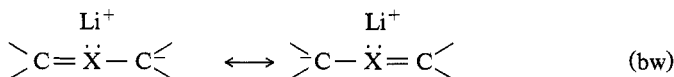
where  $\text{Y} = \text{O}$  <sup>148</sup> or  $\text{S}$  <sup>149</sup>.

3. Groups having a partially or fully charged heteroatom:



where X = S, S(O), Se, P or As. Examples of such groups are  $\text{P}(\text{O})(\text{OR})_2$ ,<sup>150-152</sup>  $\text{P}(\text{O})\text{R}_2$ ,<sup>150,151</sup>  $\text{P}(\text{S})(\text{OEt})_2$ ,<sup>153</sup>  $\text{P}(\text{O})(\text{NMe}_2)_2$ ,<sup>154</sup>  $\text{S}(\text{O})\text{R}$ ,<sup>153-156</sup>  $\text{S}(\text{O})\text{NR}_2$ ,<sup>157</sup>  $\text{S}(\text{O})_2\text{R}$ ,<sup>158</sup>  $\text{S}(=\text{NR})\text{R}$ ,<sup>159</sup>  $\text{Se}(\text{O})\text{R}$ ,<sup>160</sup> and  $\text{As}(\text{O})\text{R}_2$ .<sup>161</sup>

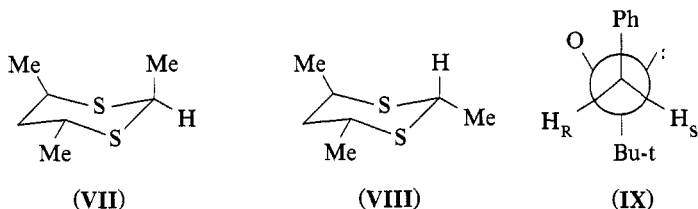
## 4. Delocalization:



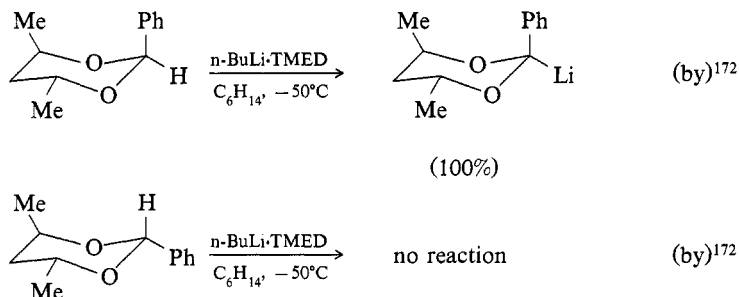
This is shown by lithiated imines, e.g.<sup>162</sup>:



Sulfur and the second-row elements have been thought to stabilize carbanions by delocalizing the negative charge into low-lying d orbitals<sup>118,125</sup>. This theory is losing favor and one based on polarization is more accepted<sup>163-168</sup>. The polarizability of the heteroatom is considered to allow diffusion of the carbanion lone pair into the carbon framework. This diffusion is higher when the carbanion lone pair (or C—Li bond) is syn-periplanar to the C—heteroatom bond. This accounts for the greater reactivity of equatorial than axial hydrogens in dithianes, [e.g., **VII** is metallated more readily than **VIII**.<sup>169-171</sup>

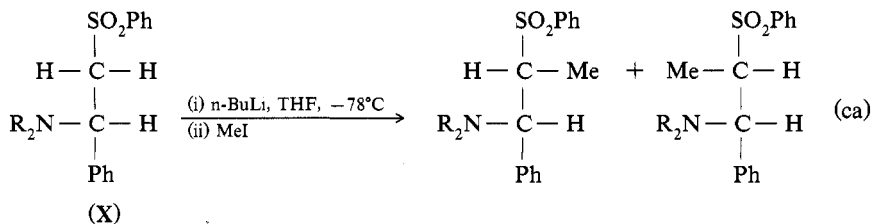


and in acetals<sup>172</sup>. The metallation of the (H-2) proton in 1,3-dioxolanes, 1,3-dioxanes and open-chain acetals is possible only if that proton can occupy an equatorial conformation, e.g.:

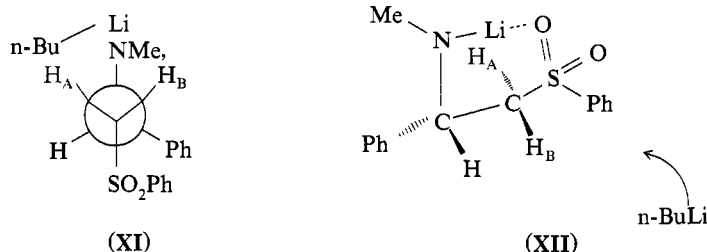


Another example is shown by the metallation<sup>173</sup> of **(IX)**, in which the relative reactivity of  $\text{H}_\text{S}:\text{H}_\text{R}$  is at least 100:1 toward MeLi in THF at  $-60^\circ\text{C}$ . Other selective lithiations include those of N-nitrosamines, which occur at the carbon syn to the nitroso oxygen, [see also Eqs. (br) and (bs)] and lithiations of oximes,  $(\text{RCH}_2)\text{RR}'=\text{NOH}$ , which provide syn- $\text{RCHLiCR}'=\text{NOLi}$  (see Table 3).

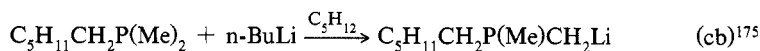
The stereochemistry of  $\text{PhCH}(\text{NR}_2)\text{CH}_2\text{SO}_2\text{Ph}$  (**X**) with  $n\text{-BuLi}$  in THF at  $-78^\circ\text{C}$  indicates involvement of the  $\text{NR}_2$  group:



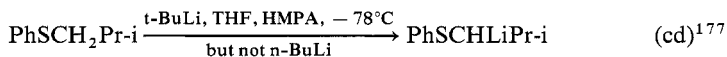
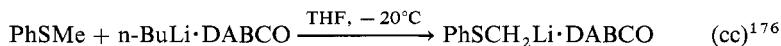
(where if  $\text{R}_2\text{N} = \text{Me}_2\text{N}$  the product ratio is 84 : 16 and if  $\text{R}_2\text{N} = \text{MeHN}$ , the product ratio is 0 : 100). The reaction of **X** ( $\text{R} = \text{Me}$ ) occurs because the  $\text{H}_\text{A}$  proton is easier to replace than  $\text{H}_\text{B}$ , owing to the compression with the  $\text{Ph}$  groups (see **XI**). For reaction of **X** ( $\text{R}_2 = \text{MeH}$ ), prior reaction at the  $\text{N-Li}$  to give (**XII**) results in the  $\text{H}_\text{B}$  proton now becoming the more accessible<sup>174</sup>:



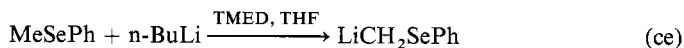
Alkyl substituents reduce the acidity of  $\alpha$  protons. This results in selected lithiations, as in:



or the necessity of using more effective lithiating agents:



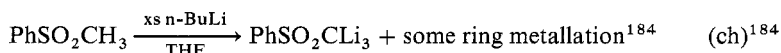
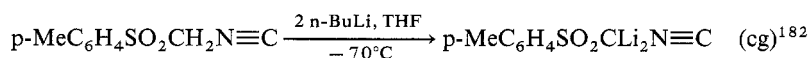
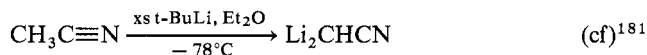
Use of  $\text{LiNR}_2$  is recommended for deprotonation of selenides ( $\text{PhSeCH}_2\text{Y}$ ) to give  $\text{PhSeCHLiY}$ , although  $t\text{-BuLi}$  can be used<sup>178</sup> with  $(\text{MeSe})_2\text{CH}_2$  and  $n\text{-BuLi} \cdot \text{TMED}$  with<sup>179</sup>  $\text{PhSeMe}$ :



However, for complete metallation,  $\text{Y}$  ought to be an activating group; e.g.,  $\text{PhSeCH}_2\text{OMe}$  is metallated only partially by  $\text{Li}$  tetramethylpiperidine ( $\text{Li} \cdot \text{TMP}$ ), whereas  $m\text{-CF}_3\text{C}_6\text{H}_4\text{SeCH}_2\text{OMe}$ , owing to the electron withdrawal of the  $\text{CF}_3$  group, reacts completely with  $\text{Li} \cdot \text{TMP}$ . Less easily metallated<sup>133</sup> than  $\text{PhSeCH}_2\text{Y}$  is  $\text{PhSeCHMeY}$ , and even cyclopropylphenylselenide is not metallated by  $\text{LiNR}_2$  in THF.

Reaction (ce) should be contrasted with the cleavage<sup>180</sup> of MeSePh to PhLi and PhSeBu-n using n-BuLi in THF.

Hetero-substituted alkanes, such as nitriles<sup>181</sup>, isocyanides<sup>182,183</sup>, sulfones<sup>184,185</sup> and sulfonamides<sup>185,186</sup> are di- or polyolithiated, e.g.:



In addition to gem-dilithiations, dilithiation at different carbons can occur, e.g.<sup>187</sup>:

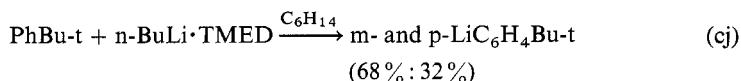


Tables 3–11 are organized according to the  $\alpha$ -heteroatom. Where there are two different hetero-substituted groups present in the carbanions, the listing in the tables is in accord with the priority sequence: N, P, O, S, Se and halogen (as heteroatoms), CO<sub>2</sub>R, CN, and metalloids. This takes no regard of the stabilizing effectiveness of the hetero-substituted groups present. Table 12 lists lithioformamides and -thioformamides.

Suitably placed hydroxyl, alkoxyl or amino groups, not in  $\alpha$  positions, can also enhance the reactivity of C–H bonds toward lithiation (e.g., as in cyclopropanes). Such enhancements arise from the intramolecular coordination of the product organolithiums<sup>403,404</sup>.

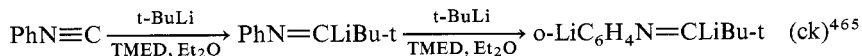
(iv) Metallation of Substituted Benzenes. As mentioned earlier, PhH is metallated by n-BuLi·TMED but not by n-BuLi in THF. Metallation of PhPh occurs more easily, e.g., using n-BuLi in Et<sub>2</sub>O or even in Et<sub>2</sub>O–hexane; the product distribution, however, is, dependent on the solvent<sup>405</sup>.

Alkylbenzenes containing benzylic hydrogens are metallated partially if not totally at such sites. Metallation of PhMe, PhEt and PhPr-*i* provides both benzylic and ring-metallated products, with the relative yields of the latter increasing in the sequence given [see Eqs. (m)–(n)]. For PhBu-*t*, which has no benzylic hydrogens, only ring metallation occurs<sup>30</sup>, the major product being the meta isomer. No ortho isomer is detected:



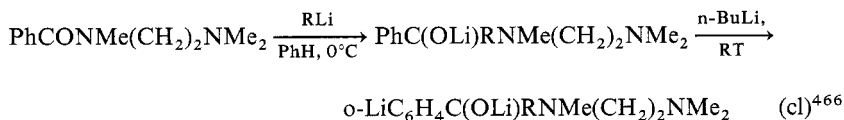
Certain functionally substituted groups in benzenoid compounds direct Li into their ortho sites<sup>406</sup>. Among these groups are: NR<sub>2</sub><sup>407–410</sup>, CH<sub>2</sub>NR<sub>2</sub><sup>411–413</sup>, CH(NR<sub>2</sub>)<sub>2</sub><sup>414</sup>, CR'<sub>2</sub>CH<sub>2</sub>NR<sub>2</sub><sup>415–417</sup>, CONR<sub>2</sub><sup>418–422</sup>, pyrazolyl<sup>423</sup>, 2-oxazoliny<sup>424–431</sup>, imines<sup>432</sup>, OR<sup>433–438</sup>, SR<sup>439</sup>, CR<sub>2</sub>OR<sup>440</sup>, CH(OMe)<sub>2</sub><sup>440–441</sup>, SO<sub>2</sub>NR<sub>2</sub><sup>442–444</sup>, SO<sub>2</sub>Ar<sup>445,446</sup>, SO<sub>2</sub>OR<sup>442</sup>, F<sup>447</sup>, Cl<sup>421</sup>, CF<sub>3</sub><sup>448</sup> and Ph<sub>2</sub>P = NPh<sup>449</sup> as well as those which have

replacable hydrogens and are themselves metallated during the course of reaction, e.g.,  $\text{NHCOBu-t}^{37}$ ,  $\text{NHCO}_2\text{Bu-t}^{450}$ ,  $\text{CONHR}^{451-455}$ ,  $\text{CSNHR}^{456}$ ,  $\text{CR}_2\text{OH}^{457-460}$ ,  $\text{CHOHCH}_2\text{NR}_2^{418}$ ,  $\text{SO}_2\text{NHR}^{461,462}$ ,  $\text{SO}_3\text{H}^{463,464}$ , and those which combine with RLi prior to ortho substitution, e.g.,  $-\text{N}\equiv\text{C}^{465}$ :



For the groups that react with RLi, 2 equiv of the lithiating agent are required to complete the ortho metallation. Table 13 lists some examples.

Amides can undergo addition reactions with RLi. Appropriate conditions must be chosen, if this is to be avoided. Use, however, is, made of these additions, e.g.:



Compounds containing ortho-directing groups are more readily metallated than is PhH irrespective of the electronic effects of the directing group. Among the ortho-directing groups are those which are electron withdrawing, resulting in enhancements of the acidity of ortho-hydrogens and facilitating metallations at the ortho sites via an acid–base mechanism. Many directing groups have donor properties and so are able to coordinate to the lithiating agent and hold it close to the ortho site. Metallation then proceeds via a coordination mechanism and occurs at the ortho site no matter what the electronic effects of the group are.

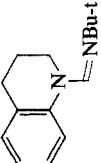
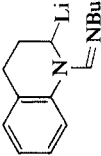
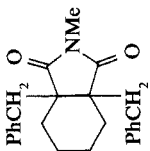
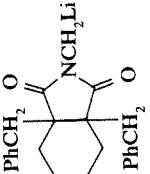
Groups acting just via their electron withdrawal include  $\text{CF}_3$ , F or Br, whereas  $\text{CR}'_2\text{NR}_2$ ,  $\text{CR}'_2\text{CH}_2\text{NR}_2$ ,  $\text{CR}'_2\text{OR}$  or  $\text{CR}'(\text{OR})_2$  act via their coordinating ability. For other ortho-directing groups, both effects operate. The acid–base and coordination mechanisms are two extremes; the relative importance for any aromatic compound depends on the groups present. Under kinetically controlled conditions, the best ortho-directing groups possess electron-releasing effects and are strong donors.

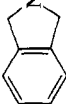

A consequence of coordination of the lithiating agent to the donor group is an enhancement of the electron withdrawal; e.g., coordination of RLi to OMe [(a –I (electron withdrawal via the inductive effect) and a + M group (electron releasing via a mesomeric effect)] weakens or nullifies the + M effect and so leaves the inductive effect to aid substitution at the ortho site. Such coordination can be monitored by spectroscopy. A donor group should be complexed within the product organolithium aggregate and so is unable to assist in further metallations. Therefore, even with xs metallating agent, only a monolithio product<sup>503</sup> is obtained from  $\text{PhCH}_2\text{NMe}_2$ .

The greater reactivity<sup>434</sup> of  $\text{PhOCH}_2\text{CH}_2\text{OMe}$  than PhOMe, arises from the stronger coordination of RLi by the two oxygens.

The ethers PhOBu-t and PhOMe are of equal reactivity despite the differences in steric hindrance to RLi. Steric retardation however, is, observed for o-substitutions to OMe in o-MeOC<sub>6</sub>H<sub>4</sub>Bu-t<sup>504</sup>, but not o-MeOC<sub>6</sub>H<sub>4</sub>Me<sup>505</sup> (using n-BuLi, t-BuLi or n-BuLi·TMED). The site of lithiation of p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub> depends on reaction conditions. Metallation with the (n-BuLi)<sub>6</sub> aggregate, a good electron-pair acceptor acid, occurs ortho to CH<sub>2</sub>NMe<sub>2</sub> (kinetic-controlled product), a consequence of coordination of n-BuLi to NMe<sub>2</sub>; in contrast the monomeric n-BuLi·TMED complex, a poor

TABLE 3. FORMATION OF  $\alpha$ -NITROGEN-SUBSTITUTED ALKYL LITHIUMS VIA LITHIATION

Compound	Lithiating conditions	Product	Refs.
$t\text{-BuN} = \text{CHN}(\text{CH}_2)_3\text{CH}_2$ $\text{C}_6\text{H}_{11}\text{N} = \text{CHNMe}_2$	$t\text{-BuLi}$ , THF, $-78^\circ\text{C}$ $t\text{-BuLi}$ , THF, $-78^\circ\text{C}$	$t\text{-BuN} = \text{CHN}(\text{CH}_2)_3\text{CHLi}$ $\text{C}_6\text{H}_{11}\text{N} = \text{CHNMeCH}_2\text{Li}$	188 189
	$t\text{-BuLi}$ , $-78^\circ\text{C}$		190
$\text{Et}_2\text{NCH}_2\text{CN}$ $2,4,6\text{-(i-Pr)}_3\text{C}_6\text{H}_2\text{COCH}_2\text{NMe}_2$ $2,4,6\text{-(i-Pr)}_3\text{C}_6\text{H}_2\text{CONMe}_2$	$\text{LiN}(\text{Pr-}i)_2$ , THF, HMPA, $-78^\circ\text{C}$ $s\text{-BuLi}$ , THF, TMED, $-78^\circ\text{C}$ $s\text{-BuLi}$ , THF, TMED, $-78^\circ\text{C}$	$\text{Et}_2\text{NCHLiCN}$ $\text{ArCOCHLiNMe}_2^a$ $\text{ArCONMeCH}_2\text{Li}^b$	191 192 193
$\text{ArC}(\text{ON}(\text{CH}_2)_3\text{CH}_2)$ $\text{PhCONHCH}_2\text{Ph}$	$s\text{-BuLi}$ : TMED, THF, $-78^\circ\text{C}$ $n\text{-BuLi}$ , $\text{LiN}(\text{Pr-}i)_2$ , diglyme	$\text{ArC}(\text{ON}(\text{CH}_2)_3\text{CHLi})$ $\text{PhCONLiCHLiPh}$	194 195
	$s\text{-BuLi}$ , THF, HMPA, $-100^\circ\text{C}$		196
$t\text{-BuC}(\text{S})\text{NMe}_2$ $\text{cis-(cyclo-C}_6\text{H}_{11}\text{NCHPhCHCOPh)}$	$s\text{-BuLi}$ , THF, TMED, $-78^\circ\text{C}$ $\text{LiNMePh}$ , $\text{C}_6\text{H}_{14}$ , $\text{Et}_2\text{O}$ , $-78^\circ\text{C}$	$t\text{-BuC}(\text{S})\text{NNMeCH}_2\text{Li}$ $\text{cis-(cyclo-C}_6\text{H}_{11}\text{NCHPhCHLiCOPh)}$	197 198
$\text{MeNCH}_2\text{CH}_2\text{CHCO}_2\text{H}$ $\text{ONNMe}_2$	$\text{LiN}(\text{Pr-}i)_2$ , THF, $0^\circ\text{C}$ $\text{LiN}(\text{Pr-}i)_2$ , THF, $-78^\circ\text{C}$	$\text{MeNCH}_2\text{CH}_2\text{CHLiCO}_2\text{Li}$ $\text{ONNMeCH}_2\text{Li}$	199 200
$\text{ONN}(\text{CH}_2)_2\text{CH}_2$ $\text{MeNC}$ $\text{MeCH}_2\text{NC}$	$\text{LiN}(\text{Pr-}i)_2$ , THF, $-78^\circ\text{C}$ $n\text{-BuLi}$ , THF, $-70^\circ\text{C}$ $\text{Li-TMP}$ , THF, $-70^\circ\text{C}$	$\text{ONN}(\text{CH}_2)_2\text{CHLi}$ $\text{LiCH}_2\text{NC}$ $\text{MeCHLiNC}$	201 202 202

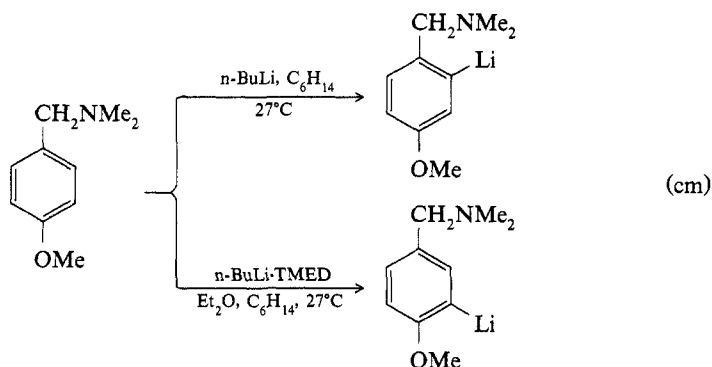
PhSCH <sub>2</sub> NC	n-BuLi, THF, –60°C	203
Chiral CH <sub>2</sub> CP <sub>2</sub> CHNC	LiN(Pr-i) <sub>2</sub> , THF, –78°C	204
p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NH(CH <sub>2</sub> ) <sub>3</sub> NC	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , –78°C	205
(Et <sub>2</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> NC	n-BuLi, THF, –70°C	206
(Me <sub>2</sub> N) <sub>2</sub> P(O)N(Me)CH <sub>2</sub> Ph	n-BuLi, Et <sub>2</sub> O, –70°C	207
(Me <sub>2</sub> N) <sub>2</sub> P(O) <sub>2</sub>	s-BuLi, DME, –78°C	208
	n-BuLi, THF, RT	209
		
$\left[ \text{CH}_2(\text{CH}_2)_2 \text{NCH}_2\text{P}(\text{O})(\text{OEt})_2 \right]_2$	n-BuLi, THF, –78°C	210
$\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CH}_2$	n-BuLi, 0°C, THF	211
$\text{Me}_2\text{C} = \text{NNMe}_2$	LiNEt <sub>2</sub> , Et <sub>2</sub> O, 0°C	212
$\text{Me}(\text{MeCH}_2)_2\text{C} = \text{NNMe}_2$	n-BuLi, –78°C, THF	213
$\text{MeC}[\text{CH}(\text{OMe})_2] = \text{NNMe}_2$	LiNEt <sub>2</sub> , HMPT, –65°C, PhH	214
$\text{PhCH}_2\text{CH} = \text{NOH}$	LiN(Pr-i) <sub>2</sub> , THF, 0°C	215
$\text{Me}_2\text{C} = \text{NOH}$	n-BuLi, THF, 0°C	216
$\text{Me}_2\text{C} = \text{CPh}_2$	LiN(Pr-i) <sub>2</sub> , THF, Et <sub>2</sub> O, –60°C	217
$\text{Me}_2\text{CHCH} = \text{NC}_6\text{H}_{11}\text{-cyclo}$	Et <sub>2</sub> NH, HMPA, PhH	218
$\left[ \text{CH}_2(\text{CH}_2)_3 \text{C} = \text{NPr-i} \right]$	LiN(Pr-i) <sub>2</sub> , THF, –20°C	219
$\text{Ph-N} = \text{NMe}$	n-BuLi, THF, –70°C	220
$\text{C}_6\text{H}_7\text{N} = \text{N}(\text{O})\text{Me}$	LiN(SiMe <sub>3</sub> ) <sub>2</sub> , THF, 0°C	221
$\text{HC}(\text{SiMe}_3)_2\text{N}_2$	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , –78°C	222
$\text{EtO}_2\text{CCHN}_2$	n-BuLi, THF, –60°C, LiN(Pr-i) <sub>2</sub>	223
$\text{MeCOCHN}_2$	Li(Pr-i) <sub>2</sub> , THF, –78°C	224
$\text{MeCH}_2\text{NO}_2$	n-BuLi, THF, HMPA, –78°C	225

\* Ar=2,4,6-(iPr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

TABLE 4. FORMATION OF  $\alpha$ -PHOSPHORUS ALKYL LITHIUMS VIA LITHIATION

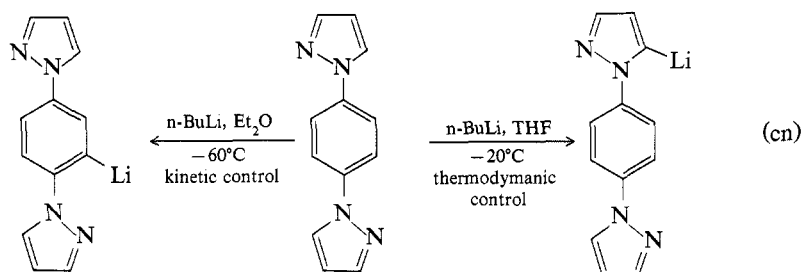
Compound	Lithiating conditions	Product	Refs.
Me <sub>3</sub> P	t-BuLi·TMED, C <sub>6</sub> H <sub>14</sub> , 20°C	Me <sub>2</sub> PCH <sub>2</sub> Li	226
MePBu-t	t-BuLi, C <sub>5</sub> H <sub>12</sub>	(t-Bu) <sub>2</sub> PCH <sub>2</sub> Li	226
MePPh <sub>2</sub>	n-BuLi·TMED, THF, 20°C	Ph <sub>2</sub> PCHLiSiMe <sub>3</sub>	227
Ph <sub>2</sub> PCH <sub>2</sub> (SiMe <sub>3</sub> ) <sub>2</sub>	n-BuLi·TMED, THF	Ph <sub>2</sub> PCLi(SiMe <sub>3</sub> ) <sub>2</sub>	228
(Me <sub>2</sub> P) <sub>2</sub> CH <sub>2</sub>	t-BuLi, C <sub>5</sub> H <sub>12</sub>	(Me <sub>2</sub> P) <sub>2</sub> CHLi	229
(Ph <sub>2</sub> P) <sub>2</sub> CH <sub>2</sub>	n-BuLi·TMED, C <sub>6</sub> H <sub>14</sub> , PhH, RT	(Ph <sub>2</sub> P) <sub>2</sub> CHLi	230
(Me <sub>2</sub> P) <sub>3</sub> CH	t-BuLi, THF, C <sub>5</sub> H <sub>12</sub>	(Me <sub>2</sub> P) <sub>3</sub> CLi	231
Ph <sub>2</sub> PCH <sub>2</sub> OMe	s-THF, -95°C	Ph <sub>2</sub> PCHLiOMe	232
CH <sub>2</sub> =PMe <sub>2</sub> N=PMe <sub>3</sub>	MeLi, Et <sub>2</sub> O, 0°C	CH <sub>2</sub> =PMe <sub>2</sub> N=PMe <sub>2</sub> CH <sub>2</sub> Li	233
[Me <sub>3</sub> PBH <sub>2</sub> PMe <sub>3</sub> ]Br	t-BuLi, THF, C <sub>5</sub> H <sub>12</sub> , -25°C	CH <sub>2</sub> =PMe <sub>2</sub> BH <sub>2</sub> PMe <sub>2</sub> CH <sub>2</sub> Li	233
Ph <sub>2</sub> P(O)Me	n-BuLi, C <sub>6</sub> H <sub>14</sub> , Et <sub>2</sub> O	Ph <sub>2</sub> P(O)CH <sub>2</sub> Li	234
C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> P(X)Ph <sub>2</sub> X = S or O	n-BuLi, Et <sub>2</sub> O, THF, RT	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CHLiP(X)Ph <sub>2</sub>	235
Ph <sub>2</sub> P(O)Pr-n	n-BuLi·TMED, THF, -78°C	Ph <sub>2</sub> P(O)CHLiEt	236
Ph <sub>2</sub> P(O)CH <sub>2</sub> SPh	n-BuLi·TMED, THF, -78°C	Ph <sub>2</sub> P(O)CHLiSPh	236
[Me <sub>2</sub> P(S)] <sub>3</sub> CH	n-BuLi, THF, -20°C	[Me <sub>2</sub> P(S)] <sub>3</sub> CLi	237
C <sub>6</sub> H <sub>11</sub> (Ph)P(S)Me	n-BuLi·TMED, THF, -78°C	C <sub>6</sub> H <sub>11</sub> (Ph)P(S)CH <sub>2</sub> Li	238
[Ph <sub>2</sub> P(O)] <sub>2</sub> CH <sub>2</sub>	n-BuLi, PhH	[Ph <sub>2</sub> P(O)] <sub>2</sub> CHLi	239
(MeO) <sub>2</sub> P(O)Me	n-BuLi, THF, -78°C	(MeO) <sub>2</sub> P(O)CH <sub>2</sub> Li	240
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> SMe	n-BuLi, THF, -70°C	(EtO) <sub>2</sub> CHLiSMe	241
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> Cl	n-BuLi, THF, -78°C	(EtO) <sub>2</sub> P(O)CHLiCl	242
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> CN	n-BuLi, THF	(EtO) <sub>2</sub> P(O)CHLiCN	243
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> CO <sub>2</sub> Me	n-BuLi, THF	(EtO) <sub>2</sub> P(O)CHLiCO <sub>2</sub> Me	244
(PhCH <sub>2</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CO <sub>2</sub> H	2 equiv. LiN(Pr-i) <sub>3</sub> , THF, -80°C	(PhCH <sub>2</sub> O) <sub>2</sub> P(O)CHLiCO <sub>2</sub> Li	245
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> SO <sub>2</sub> Me	n-BuLi, THF, -78°C	(EtO) <sub>2</sub> P(O)CHLiSO <sub>2</sub> Me	246
(Me <sub>2</sub> N) <sub>2</sub> P(O)Me	n-BuLi, THF, -78°C	(Me <sub>2</sub> N) <sub>2</sub> P(O)CH <sub>2</sub> Li	247
(Me <sub>2</sub> N) <sub>2</sub> P(O)CH <sub>2</sub> Cl	n-BuLi, THF, -78°C	(Me <sub>2</sub> N) <sub>2</sub> P(O)CHLiCl	242
(MeO) <sub>2</sub> P(S)Me	n-BuLi, THF, -78°C	(MeO) <sub>2</sub> P(S)CH <sub>2</sub> Li	240
(EtO) <sub>2</sub> P(S)CH <sub>2</sub> Cl	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , -70°C	(EtO) <sub>2</sub> P(S)CHLiCl	248

electron-pair acceptor acid, attacks at the most acidic ring position, ortho to the MeO group<sup>506</sup> (thermodynamic product, e.g.:

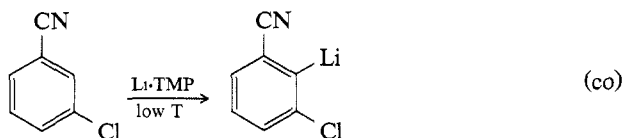




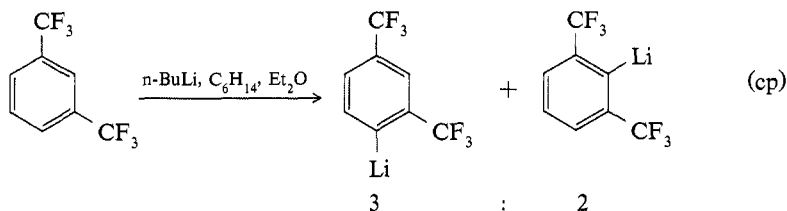
Kinetic and thermodynamic products also are obtained with 1,4-phenylene di-(1-pyrazole), e.g.<sup>507</sup>:



In metallations<sup>406</sup> of 1,2-, 1,3-, 1,4- and more highly substituted compounds, the sites of lithiation (under kinetic-controlled conditions) are governed by the relative ortho-directing abilities of the groups present. For 1,3-compounds, lithiation occurs to the greatest extent at the 2-position if both groups are ortho directors, even weak ortho-directing groups; e.g., see Eq. (co)<sup>406</sup>. For lithiation of *m*-CNC<sub>6</sub>H<sub>4</sub>Cl, the use of the nonnucleophilic Li·TMP and low T are required to avoid reaction with either substituent:



Exceptions are *m*-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub><sup>508</sup> and *m*-(*n*-BuNHCO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub><sup>406</sup>. For *m*-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, metallation occurs more at the 4-position:



There are no steric problems to attack occurring between the two groups; however, steric effects may be important in *m*-RXC<sub>6</sub>H<sub>4</sub>YR' (X, Y = O or S)<sup>509</sup>. The Me group has only a little ortho-directing ability, and 3-MeC<sub>6</sub>H<sub>4</sub>OMe is metallated<sup>510</sup>:

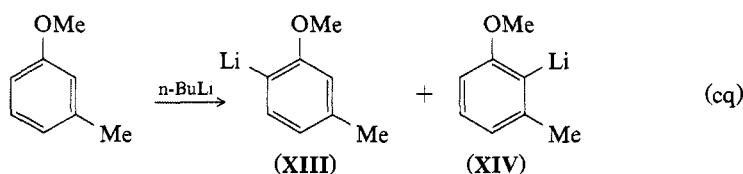


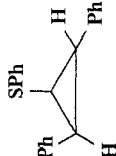
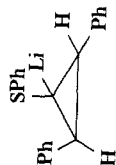
TABLE 5. FORMATION OF  $\alpha$ -OXYGEN-SUBSTITUTED ALKYL LITHIUMS VIA LITHIATION

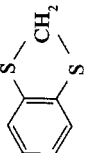
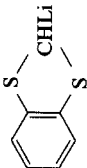


Compound	Lithiating conditions	Product	Refs.
$\text{Me}_3\text{SiCH}_2\text{OMe}$ $\text{PhCH}_2\text{OMe}$	s-BuLi, THF, $-70^\circ\text{C}$ n-BuLi-TMED, $\text{C}_6\text{H}_{14}$ , $-10^\circ\text{C}$	$\text{Me}_3\text{SiCHLiOMe}$ $\text{PhCHLiOMe}$	249 250
	n-BuLi, or LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-45^\circ\text{C}$	$\text{ArCLi(OMe)}_2$	251
	n-BuLi, or LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-45^\circ\text{C}$		251
$\text{PhSCH}_2\text{OMe}$ $\text{m-CF}_3\text{C}_6\text{H}_4\text{SeCH}_2\text{OMe}$ $\text{PhSO}_2\text{CH}_2\text{OMe}$ $\text{S(CH}_2)_3\text{OCHMMMe}_3$ M = Si or Ge	n-BuLi, THF, $-30^\circ\text{C}$ Li-TMP, <sup>a</sup> THF, $-78^\circ\text{C}$ n-BuLi, THF, $-70^\circ\text{C}$ s-BuLi, THF, $-78^\circ\text{C}$	$\text{PhSCHLiOMe}$ $\text{m-CF}_3\text{C}_6\text{H}_4\text{SeCHLiOMe}$ $\text{PhSO}_2\text{CHLiOMe}$ $\text{S(CH}_2)_3\text{OCLiMMMe}_3$	252 253 254 255
$\text{PhOCH}_2\text{CO}_2\text{H}$ $(\text{PhO})_2\text{CHCO}_2\text{H}$ $(\text{MeO})_2\text{CHCO}_2\text{Me}$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$ LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$ LiN(Bu- <i>i</i> ) <sub>2</sub> , THF, $-70^\circ\text{C}$	$\text{PhOCHLiCO}_2\text{Li}$ $(\text{PhO})_2\text{CHLiCO}_2\text{Li}$ $(\text{MeO})_2\text{CHLiCO}_2\text{Me}$	256 256 257

(MeO) <sub>2</sub> CHCN	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , HMPA, –78°C	(MeO) <sub>2</sub> CLiCN	258
2,4,6-(Pr-i) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> C(O)OMe	s-BuLi, THF, TMED, –95°C	2,4,6-(i-Pr) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> C(O)OCH <sub>2</sub> Li	259
PhSCH(OMe)SiMe <sub>3</sub>	s-BuLi-TMED, THF, –78°C	PhSCLi(OMe)SiMe <sub>3</sub>	260
Ph <sub>3</sub> SiCHCH <sub>2</sub> O	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , –78°C	Ph <sub>3</sub> SiCLiCH <sub>2</sub> O	261
PhSO <sub>2</sub> CHCH <sub>2</sub> O	n-BuLi, THF, –78°C	PhSO <sub>2</sub> CLiCH <sub>2</sub> O	262
(EtO) <sub>2</sub> P(O)CHCHPhO	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , Et <sub>2</sub> O, –110°C	(EtO) <sub>2</sub> P(O)CLiCHPhO	262
N ≡ CCHCHMeO	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , Et <sub>2</sub> O, –110°C	N ≡ CCLiCHMeO	262
EtO <sub>2</sub> CCHCH(CO <sub>2</sub> Et)O	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , Et <sub>2</sub> O, –110°C	EtO <sub>2</sub> CCLiCH(CO <sub>2</sub> Et)O	262
PhCHCH <sub>2</sub> O	t-BuLi, THF, –95°C to –50°C	PhCLiCH <sub>2</sub> O	262
CMe <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> SO <sub>2</sub>	n-BuLi, THF, –80°C	CMe <sub>3</sub> CH <sub>2</sub> OCHLiSO <sub>2</sub>	263
(EtO) <sub>2</sub> P(O)CRHOSiMe <sub>3</sub>	LiN(Pr-i) <sub>2</sub> , THF, –78°C	(EtO) <sub>2</sub> P(O)CRLi(OSiMe <sub>3</sub> )	264,265
R = alkyl or aryl		(EtO) <sub>2</sub> P(O)C(SiMe <sub>3</sub> )OLi	
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> OCH(OCH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, –78°C	(EtO) <sub>2</sub> P(O)CHLiOCH(OCH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>	266
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OMe	LiN(Pr-i) <sub>2</sub> , THF, –78°C	(EtO) <sub>2</sub> P(O)CHLiOCH <sub>2</sub> CH <sub>2</sub> OMe	266
PhCHCN(OSiMe <sub>3</sub> )	LiN(Pr-i) <sub>2</sub> , THF, –78°C	PhCLiCN(OSiMe <sub>3</sub> )	267,268

<sup>a</sup> Li-TMP = Li tetramethylpiperidine

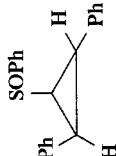
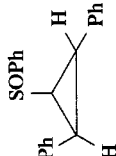
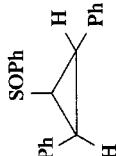
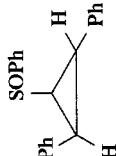
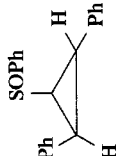
TABLE 6. FORMATION OF  $\alpha$ -SULFUR ALKYL LITHIUMS VIA LITHIATION

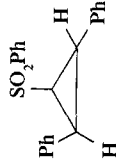
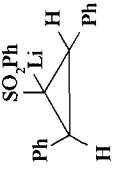
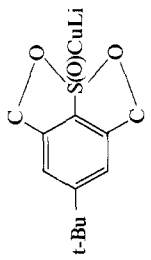
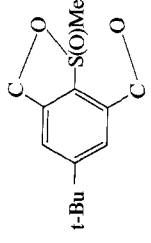
Compound	Lithiating conditions	Product	Refs.
$\text{Me}_2\text{S}$	$n\text{-BuLi}\cdot\text{TMED}$ , hexane, $20^\circ\text{C}$	$\text{MeSCH}_2\text{Li}$	269
$\text{PhSMe}$	$n\text{-BuLi}\cdot\text{DABCO}^a$ , THF, $0^\circ\text{C}$ $\text{PhLi}$ , THF, $25^\circ\text{C}$	$\text{PhSCH}_2\text{Li}$	270 270
$\text{PhSCH}_2\text{CHMe}_2$	$t\text{-BuLi}$ , THF, HMPA, $-78^\circ\text{C}$	$\text{PhSCHLiCHMe}_2$	271
$\text{PhCH}_2\text{SH}$	$t\text{-BuLi}$ , THF, HMPA, $-78^\circ\text{C}$	$\text{PhCHLiSH}$	272
$\text{PhSCH}_2\text{Ph}$	$n\text{-BuLi}\cdot\text{TMED}$ , THF, $0^\circ\text{C}$	$\text{PhSCHLiPh}$	273
$\text{PhCH}_2\text{SCH}_2\text{Ph}$	$n\text{-BuLi}$ , THF, DABCO <sup>a</sup>	$\text{PhCHLiSCH}_2\text{Ph}$	274
$\text{PhSCHCH}_2\text{CH}_2$	$n\text{-BuLi}\cdot\text{TMED}$ , THF, $-78^\circ\text{C}$	$\text{PhSCHLiCH}_2\text{CH}_2$	275
$\text{PhCOC(Et)} = \text{C(SMe)}_2$	$\text{LiN(Pr-}i\text{)}_2$ , HMPA, THF, $-78^\circ\text{C}$	$\text{PhCOC(Et)} = \text{C(SMe)SCH}_2\text{Li}$	276
$\text{PhN} = \text{C(SMe)}_2$	$\text{LiN(Pr-}i\text{)}_2$ , THF, $\text{C}_6\text{H}_{14}$ , $-70^\circ\text{C}$	$\text{PhN} = \text{C(SMe)SCH}_2\text{Li}$	277
$2,4,6\text{-Et}_3\text{C}_6\text{H}_2\text{C(O)SMe}$	$\text{Li}\cdot\text{TMP}^b$ , THF, $-78^\circ\text{C}$	$2,4,6\text{-Et}_3\text{C}_6\text{H}_2\text{C(O)SCH}_2\text{Li}$	278
$\text{CH(Pr-}i\text{-an)(CH}_2\text{)}_2\text{CH(Me-cis)(CH}_2\text{)CHOC(O)SMe}$	$\text{LiN(Pr-}i\text{)}_2$ , THF, $-78^\circ\text{C}$	$\text{ROC(O)SCH}_2\text{Li}^c$	279
$\text{HSCH}_2\text{CO}_2\text{Et}$	$\text{LiN(Pr-}i\text{)}_2$ , TMED, THF, $-78^\circ\text{C}$	$\text{LiSCHLiCO}_2\text{Et}$	280
$\text{PhSCH}_2\text{SiMe}_3$	$n\text{-BuLi}\cdot\text{TMED}$ , $\text{C}_6\text{H}_{14}$ , $0^\circ\text{C}$	$\text{PhSCHLiSiMe}_3$	281
$\text{PhSCHPhSiMe}_3$	$n\text{-BuLi}\cdot\text{TMED}$ , $\text{C}_6\text{H}_{14}$ , $0^\circ\text{C}$	$\text{PhSCHLiPhSiMe}_3$	282
$\text{PhSCH}_2\text{CN}$	$\text{LiN(Pr-}i\text{)}_2$ , THF, $-78^\circ\text{C}$	$\text{PhSCHLiCN}$	283
$\text{PhSCH}_2\text{CO}_2\text{H}$	$\text{LiN(Pr-}i\text{)}_2$ , THF, $0^\circ\text{C}$	$\text{PhSCHLiCO}_2\text{Li}$	284
$\text{PhSCH}_2\text{CO}_2\text{Me}$	$\text{LiN(Pr-}i\text{)}_2$ , THF, $-60^\circ\text{C}$	$\text{PhCHLiCO}_2\text{Me}$	285
$(\text{RO})_2\text{P(O)SCR}^d\text{HCO}_2\text{Et}$	$\text{LiN(Pr-}i\text{)}_2$	$(\text{RO})_2\text{P(O)SCR}^d\text{LiCO}_2\text{Et}$	286
	$n\text{-BuLi}$ , THF, $-20^\circ\text{C}$		287

(MeS) <sub>2</sub> CH <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , HMPA, -78°C	288	(MeS) <sub>2</sub> CHLi		288
(MeS) <sub>2</sub> CHSnMe <sub>3</sub>	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , HMPA, -78°C	288	(MeS) <sub>2</sub> ClSnMe <sub>3</sub>		289
(PhS) <sub>2</sub> CHMe	n-BuLi-TMED	289	(PhS) <sub>2</sub> CLiMe		290,291
(PhS) <sub>2</sub> CH	n-BuLi, THF, -78°C	291	(PhS) <sub>2</sub> CLi		292
[Et <sub>2</sub> NC(S) <sub>2</sub> CH <sub>2</sub> ] MeSCHLiSC(S)NMe <sub>2</sub>	n-BuLi, THF, -78°C n-BuLi, THF, -55°C	291 292	[Et <sub>2</sub> NC(S) <sub>2</sub> CHLi MeSCHLiSC(S)NMe <sub>2</sub>		293
	n-BuLi, THF, -30°C	293			293
	n-BuLi, THF, -30°C	294			294
$\left[ \text{S}(\text{CH}_2)_3\text{SCH}_2 \right]$	n-BuLi, THF, -40°C	295	$\left[ \text{S}(\text{CH}_2)_3\text{SCHLi} \right]$		295
$\left[ \text{S}(\text{CH}_2)_3\text{SCHMe} \right]$	n-BuLi, C <sub>6</sub> H <sub>14</sub> , cyclo-C <sub>6</sub> H <sub>12</sub> , TMED, -20°C	296	$\left[ \text{S}(\text{CH}_2)_3\text{SCHLiMe} \right]$		296
$\left[ \text{S}(\text{CH}_2)_3\text{SCHSiMe}_3 \right]$	n-BuLi, THF, -23°C	297	$\left[ \text{S}(\text{CH}_2)_3\text{SCHLi SiMe}_3 \right]$		297
$\left[ \text{S}(\text{CH}_2)_3\text{SCHCN} \right]$	n-BuLi, THF, -40°C	298	$\left[ \text{S}(\text{CH}_2)_3\text{SCHLiCN} \right]$		298
$\left[ \text{SCH}_2\text{NMeCH}_2\text{SCH}_2 \right]$	n-BuLi, THF, -78°C	299	$\left[ \text{SCH}_2\text{NMeCH}_2\text{SCHLi} \right]$		299
$\left[ \text{SCH}_2\text{S}(\text{CH}_2)_n\text{SCH}_2 \right]$ n = 1 or 2	n-BuLi, THF, -30°C	300,301	$\left[ \text{SCH}_2\text{S}(\text{CH}_2)_n\text{SCHLi} \right]$		300,301
$\left[ \text{SCH}=\text{CHCH}=\text{CHSCH}_2 \right]$	n-BuLi, THF, -40°C	302	$\left[ \text{SCH}=\text{CHCH}=\text{CHSCHLi} \right]$		302
Me <sub>2</sub> SO	n-BuLi, THF, 0°C	303	MeSOCH <sub>2</sub> Li		303
MeS(O)Bu-t	MeLi, THF, -60°C	304	t-BuSOCH <sub>2</sub> Li		304
PhSOMe	MeLi, THF, -78°C	305	PhSOCH <sub>2</sub> Li		305

(continued)

TABLE 6. (Continued)

Compound	Lithiating conditions	Product	Refs.
$\text{PhSOCH}_2\text{CH}_3$ $\text{PhCH}_2\text{SOMe}$	$\text{MeLi}$ , THF, $-60^\circ\text{C}$ $n\text{-BuLi}$ , THF, $-70^\circ\text{C}$	$\text{PhSOCHLiMe}$ $\text{PhCHLiSOMe}$	306 307, 308
$\text{PhSOCH}_2\text{SiMe}_3$ SOPh 	$\text{MeLi}$ , THF, $-60^\circ\text{C}$ $n\text{-BuLi}$ , THF, $-70^\circ\text{C}$	$\text{PhSOCHLiSiMe}_3$	309 310
$t\text{-BuSOCHMe}_2$ 	$n\text{-BuLi}$ , THF, $-30^\circ\text{C}$		287
$t\text{-BuSOCHMe}_2$	$\text{MeLi}$ , THF, $-60^\circ\text{C}$	$t\text{-BuSOCHLiMe}_2$	304
	$\text{MeLi}$ , THF, $-78^\circ\text{C}$		311
$\text{MeSCH}_2\text{SOMe}$ $\left[\text{CH}_2(\text{CH}_2)_4\text{C}(\text{SMe})\text{SOMe}\right]$ $\left[\text{S}(\text{CH}_2)_3\text{S}(\text{O})\text{CH}_2\right]$ $\text{PhSOCH}_2\text{Cl}$ $\text{MeSONMe}_2$ $p\text{-MeC}_6\text{H}_4\text{NHSOMe}$	$n\text{-BuLi}$ , $\text{C}_6\text{H}_{14}$ , THF, $-20^\circ\text{C}$ $\text{LiNEt}_2$ , THF, $-15^\circ\text{C}$ $n\text{-BuLi}$ , THF, $\text{C}_5\text{H}_{12}$ , $-10^\circ\text{C}$ $\text{LiN}(\text{Pr}-i)_2$ , THF, $-78^\circ\text{C}$ $n\text{-BuLi}$ , THF, $-90^\circ\text{C}$ $n\text{-BuLi}$ , THF, $-78^\circ\text{C}$	$\text{MeSCHLiSOMe}$ $\left[\text{CH}_2(\text{CH}_2)_4\text{C}(\text{SMe})\text{SOCH}_2\text{Li}\right]$ $\left[\text{S}(\text{CH}_2)_3\text{S}(\text{O})\text{CHLi}\right]$ $\text{PhSOCHLiCl}$ $\text{Me}_2\text{NSOCH}_2\text{Li}$ $p\text{-MeC}_6\text{H}_4\text{NLSOCH}_2\text{Li}$	312 313 314 315 316 316
$(\text{CO})_3\text{M}[\text{CH}=\text{CPhCH}=\text{S}(\text{O})\text{Me}]$ $\text{M} = \text{Cr, Mo or W}$ $\text{PhS}(\text{O})\text{CH}_2\text{I}$	$n\text{-BuLi}$ , THF, $-70^\circ\text{C}$ $\text{LiN}(\text{Pr}-i)_2$ , THF, $-78^\circ\text{C}$	$(\text{CO})_3\text{M}[\text{CH}=\text{CPhCH}=\text{CPhCH}=\text{S}(\text{O})\text{CH}_2\text{Li}]$ $\text{PhS}(\text{O})\text{CHLiI}$	317 318

Me <sub>2</sub> NS(O) <sub>2</sub> Me	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , 0°C	Me <sub>2</sub> NS(O) <sub>2</sub> CH <sub>2</sub> Li	322
PhSO <sub>2</sub> Me	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , RT	PhSO <sub>2</sub> CHLi <sub>2</sub> +PhSO <sub>2</sub> CLi <sub>3</sub>	319, 320
n-BuSO <sub>2</sub> Bu-n	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , RT	(C <sub>3</sub> H <sub>7</sub> CHLi) <sub>2</sub> SO <sub>2</sub>	321
	LiN(Pr-i) <sub>2</sub> , THF, -20°C		287
PhCH(NMe <sub>2</sub> )CH <sub>2</sub> SO <sub>2</sub> Ph	n-BuLi, THF, -78°C	PhCH(NMe <sub>2</sub> )CHLiSO <sub>2</sub> Ph	323
<u>SO<sub>2</sub>NMe(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub></u>	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , 25°C	<u>SO<sub>2</sub>NMe(CH<sub>2</sub>)<sub>3</sub>CHLi</u>	324
<u>S(O)<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub></u>	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , 25°C	<u>S(O)<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>CHLi</u>	325
PhCH <sub>2</sub> COCH <sub>2</sub> SO <sub>2</sub> Ph	LiN(Pr-i) <sub>2</sub> , glyme, -55°C	PhCHLiCOCHLiSO <sub>2</sub> Ph	326
	n-BuLi, THF, -78°C		327
PhS(O)(=NMe)Me	n-BuLi, THF, 0°C	PhS(O)(=NMe)CH <sub>2</sub> Li	328
MeS(O)(=NTos)Me	n-BuLi, DMSO, 20°C	MeS(O)(=NTos)CH <sub>2</sub> Li	329
PhS(O)(=NTos)Me	n-BuLi, THF, -78°C	PhS(O)(=NTos)CH <sub>2</sub> Li	329
PhS(O)(=NCO <sub>2</sub> Me)Me	LiN(Pr-i)cyclo-C <sub>6</sub> H <sub>11</sub> , THF, -70°C	PhS(O)(=NCO <sub>2</sub> Me)CH <sub>2</sub> Li	330

<sup>a</sup> DABCO = 1,4-diazabicyclo[2.2.2]octane.

<sup>b</sup> Li-TMP = Li tetramethylpiperidine.

<sup>c</sup> R = CH(Pr-i-trans)(CH<sub>2</sub>)<sub>2</sub>CH(Me-cis)CH<sub>2</sub>CH.

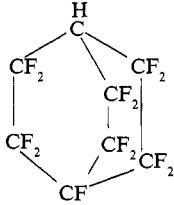
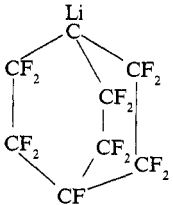
TABLE 7. FORMATION OF  $\alpha$ -SELENIUM ALKYLITHIUMS VIA LITHIATION

Compound	Lithiation conditions	Product	Refs.
PhSeMe	n-BuLi-TMED, THF, 0°C	PhSeCH <sub>2</sub> Li	331
PhSeCH <sub>2</sub> Ph	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSeCHLiPh	332
PhSeCH <sub>2</sub> SiMe <sub>3</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSeCHLiSiMe <sub>3</sub>	333, 334
PhSeCH <sub>2</sub> COPh	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSeCHLiCOPh	334
PhSeCH(CN)C <sub>6</sub> H <sub>13</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSeCLi(CN)C <sub>6</sub> H <sub>13</sub>	335
PhSeCH <sub>2</sub> CO <sub>2</sub> H	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSeCHLiCO <sub>2</sub> Li	336
PhSeCH <sub>2</sub> CO <sub>2</sub> Me	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSeCHLiCO <sub>2</sub> Me	337
C(O)O(CH <sub>2</sub> ) <sub>3</sub> CHSePh	LiN(Pr-i) <sub>2</sub> , THF, -78°C	C(O)O(CH <sub>2</sub> ) <sub>3</sub> CLiSePh	337
m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeMe	Li-TMP <sup>a</sup> , THF, -55°C	m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> Li	336
m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> SiMe <sub>3</sub>	Li-TMP <sup>a</sup> , THF, -40°C	m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCHLiSiMe <sub>3</sub>	336
PhSe(O)Me	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CH <sub>2</sub> Li	332
PhSe(O)CHMe <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CLiMe <sub>2</sub>	338
PhSe(O)CH <sub>2</sub> Ph	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CHLiPh	332, 338
PhSe(O)CH <sub>2</sub> CH <sub>2</sub> Ph	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CHLiCH <sub>2</sub> Ph	338
PhSe(O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Ph	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CHLiCH <sub>2</sub> CH <sub>2</sub> Ph	332
PhSe(O)CHMeCH(CH <sub>2</sub> ) <sub>2</sub> CH = CHCH <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CLiMeCH(CH <sub>2</sub> ) <sub>2</sub> CH = CHCH <sub>2</sub>	338
PhSe(O)CH <sub>2</sub> CH <sub>2</sub> C ≡ CMe	LiN(Pr-i) <sub>2</sub> , THF, -78°C	PhSe(O)CHLiCH <sub>2</sub> C ≡ CMe	338
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> Se(O)C <sub>8</sub> H <sub>17</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> Se(O)CHLiC <sub>7</sub> H <sub>15</sub>	336
(PhSe) <sub>2</sub> CH <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	(PhSe) <sub>2</sub> CHLi	334
(PhSe) <sub>2</sub> CHC <sub>6</sub> H <sub>13</sub>	Li-TMP <sup>a</sup> , THF, HMPA	(PhSe) <sub>2</sub> CLiC <sub>6</sub> H <sub>13</sub>	339
(PhSe) <sub>2</sub> CH	LiN(Bu-i) <sub>2</sub> , THF, -78°C	(PhSe) <sub>2</sub> CLi	331
m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCH <sub>2</sub> OMe	Li-TMP <sup>a</sup> , THF, -78°C	m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SeCHLiOMe	336

<sup>a</sup> Li-TMP = Li tetramethylpiperidine.



TABLE 8. FORMATION OF  $\alpha$ -HALOSUBSTITUTED ALKYL LITHIUMS VIA LITHIATION

Compound	Lithiating conditions	Product	Refs.
$\text{Me}_3\text{SiCH}_2\text{Cl}$	$\text{LiN}(\text{Pr}-i)_2$ , THF	$\text{Me}_3\text{SiCHLiCl}$	340
	<i>s</i> -BuLi, TMED, THF, $-78^\circ\text{C}$		341
$(p\text{-FC}_6\text{H}_4)_2\text{Me}_2\text{SiCH}_2\text{Cl}$	$\text{LiN}(\text{Pr}-i)_2$ , THF	$(p\text{-FC}_6\text{H}_4)_2\text{Me}_2\text{SiCHLiCl}$	340
$\text{Me}_3\text{SiCHClCO}_2\text{Bu}-t$	$\text{LiN}(\text{Pr}-i)_2$ , THF, $-78^\circ\text{C}$	$\text{Me}_3\text{SiCLiClCO}_2\text{Bu}-t$	342
$\text{CH}_2\text{Cl}_2$	<i>n</i> -BuLi, TMED, THF, $\text{Et}_2\text{O}$ , $-90^\circ\text{C}$	$\text{LiCHCl}_2$	343
	<i>n</i> -BuLi, THF, $\text{C}_6\text{H}_{14}$ , $-95^\circ\text{C}$		344
$\text{MeCHCl}_2$	<i>n</i> -BuLi, TMED, THF, $\text{Et}_2\text{O}$ , $-90^\circ\text{C}$	$\text{MeCLiCl}_2$	343
$\text{PhCHCl}_2$	<i>n</i> -BuLi, THF, $\text{C}_6\text{H}_{14}$ , $-90^\circ\text{C}$		344
$\text{Me}_3\text{SiCCl}_2\text{H}$	$\text{LiN}(\text{Pr}-i)_2$ , THF, $-78^\circ\text{C}$	$\text{Me}_3\text{SiCCl}_2\text{Li}$	345
$\text{EtO}_2\text{CCHCl}_2$	$\text{LiNEt}_2$ , THF, PhH, HMPA, $-78^\circ\text{C}$	$\text{EtO}_2\text{CCLiCl}_2$	346
$\text{CHCl}_3$	<i>n</i> -BuLi, THF, $\text{Et}_2\text{O}$ , petroleum ether, $-108^\circ\text{C}$	$\text{LiCCl}_3$	347
$\text{CH}_2\text{Br}_2$	$\text{LiN}(\text{Pr}-i)_2$ , $\text{Et}_2\text{O}$ , THF, $-90^\circ\text{C}$	$\text{LiCHBr}_2$	348
<i>n</i> -BuCHBr <sub>2</sub>	$\text{LiN}(\text{Pr}-i)_2$ , $\text{Et}_2$ , THF, $-90^\circ\text{C}$	<i>n</i> -BuCLiBr <sub>2</sub>	348
$\text{Me}_3\text{SiCHBr}_2$	$\text{LiN}(\text{Pr}-i)_2$ , $\text{Et}_2\text{O}$ , THF, $-80^\circ\text{C}$	$\text{Me}_3\text{SiCLiBr}_2$	348
$\text{CHBr}_3$	$\text{LiN}(\text{Pr}-i)_2$ , $\text{Et}_2\text{O}$ , THF, $-110^\circ\text{C}$	$\text{LiCBr}_3$	348
$(\text{F}_3\text{C})_3\text{CCF}_2\text{H}$	$\text{MeLi}$ , RH, $\text{Et}_2\text{O}$ , $-50^\circ\text{C}$	$(\text{F}_3\text{C})_3\text{CCF}_2\text{Li}$	349
	$\text{MeLi}$ , $\text{Et}_2\text{O}$ , $-50^\circ\text{C}$		350

The relative yields, **XIII**:**XIV**, depend on the size of the *n*-BuLi aggregate, e.g., [**XIV**]:[**XIII**] decreases in the sequence (*n*-BuLi)<sub>6</sub> in hydrocarbon (9:1) > (*n*-BuLi)<sub>4</sub> in hydrocarbon > (*n*-BuLi)<sub>2</sub> in  $\text{Et}_2\text{O}$  > monomeric *n*-BuLi·TMED (13:12).

Sequences of ortho-directing abilities are established from competition reactions. When *p*-YC<sub>6</sub>H<sub>4</sub>OMe and *n*-BuLi are combined in hexane at RT, the directing ability is ordered<sup>506</sup>: Y = SO<sub>2</sub>NMe, SO<sub>2</sub>NHMe, CONHMe, CH<sub>2</sub>NMe<sub>2</sub>, OMe, CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, NMe<sub>2</sub>, CF<sub>3</sub>, F; and when YC<sub>6</sub>H<sub>4</sub>CONEt<sub>2</sub> is used with *s*-BuLi·TMED in THF at  $-100^\circ\text{C}$ , Y = CONEt<sub>2</sub> is superior<sup>421</sup> to SO<sub>2</sub>NR<sub>2</sub>, 2-oxazolinyl, OMe, CH<sub>2</sub>NMe<sub>2</sub>, Cl, CO<sub>2</sub>H or Me. From intermolecular competition of Ph-oxazoline and PhY with *n*-BuLi at low T, the sequence is<sup>431</sup>: SO<sub>2</sub>NMe<sub>2</sub>, SO<sub>2</sub>NHMe, CON(Pr-*i*)<sub>2</sub>, CONEt<sub>2</sub> > 2-oxazolinyl > CONHMe > CH<sub>2</sub>NMe<sub>2</sub>. Discrepancies occur, and, as shown for *p*-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe, the products may depend on the lithiating agent and conditions.

Polyfluoro- and chlorobenzenes are acidic compounds; e.g.,  $\text{pK}_a$ s of C<sub>6</sub>F<sub>5</sub>H, C<sub>6</sub>Cl<sub>5</sub>H and PhH are 23, 30.5 and 37, respectively<sup>406</sup>. They can be metallated at sites ortho to the halogen. Although such products undergo elimination of LiX to give benzynes, they can be prepared in good yield at low T, e.g., below  $-50^\circ\text{C}$  for *o*-FC<sub>6</sub>H<sub>4</sub>Li; however, the Cl analogue, *o*-ClC<sub>6</sub>H<sub>4</sub>Li, decomposes<sup>511</sup> in  $\text{Et}_2\text{O}$  below  $-60^\circ\text{C}$ . Not only is metallation

TABLE 9. FORMATION OF  $\alpha$ -CARBONYL ALKYL LITHIUMS VIA LITHIATION



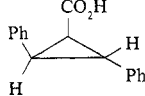
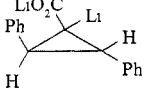
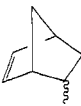
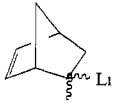
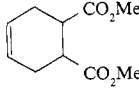
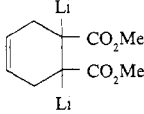
Compound	Lithiating conditions	Product	Refs
MeCO <sub>2</sub> Bu-t	LiN(Pr-i) <sub>2</sub> , C <sub>6</sub> H <sub>14</sub> , -78°C	LiCH <sub>2</sub> CO <sub>2</sub> Bu-t	351
MeCH <sub>2</sub> CO <sub>2</sub> Me	Ph <sub>3</sub> CLi, THF, -10°C	MeCHLiCO <sub>2</sub> Me	352
	LiN(Pr-i) <sub>2</sub> , THF, 0°C		353
n-BuCH <sub>2</sub> CO <sub>2</sub> H	LiN(Pr-i) <sub>2</sub> , THF, HMPA, -78°C	n-BuCHLiCO <sub>2</sub> Li	354
Me <sub>3</sub> SiCH <sub>2</sub> CO <sub>2</sub> Et	LiN(C <sub>6</sub> H <sub>11</sub> -cyclo) <sub>2</sub> , THF, -78°C	Me <sub>3</sub> SiCHLiCO <sub>2</sub> Et	355
Cl <sub>2</sub> CHCO <sub>2</sub> H	LiN(Pr-i) <sub>2</sub> , THF, 78°C	Cl <sub>2</sub> CLiCO <sub>2</sub> Li	356
Me <sub>3</sub> SiCH <sub>2</sub> CO <sub>2</sub> Bu-t	LiN(Pr-i) <sub>2</sub> , THF, -78°C	Me <sub>3</sub> SiCHLiCO <sub>2</sub> Bu-t	357
PhCH <sub>2</sub> CO <sub>2</sub> H	n-BuLi, THF, -40°C	PhCHLiCO <sub>2</sub> Li	358
(Me <sub>3</sub> Si) <sub>2</sub> CHCO <sub>2</sub> Bu-t	LiN(Pr-i) <sub>2</sub> , THF, -78°C	(Me <sub>3</sub> Si) <sub>2</sub> CHLiCO <sub>2</sub> Bu-t	359
	LiN(Pr-i) <sub>2</sub> , THF, -78°C		360
	LiN(Pr-i) <sub>2</sub> , THF, -75°C		361
MeCH(CO <sub>2</sub> H) <sub>3</sub>	n-BuLi, THF, 0°C	MeCLi(CO <sub>2</sub> Li) <sub>2</sub>	362
CH <sub>2</sub> (CO <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub>	n-BuLi, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , -60°C	LiCH(CO <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub>	363
	LiN(Pr-i) <sub>2</sub> , THF, -78°C		364
Ph <sub>3</sub> P=C(CO <sub>2</sub> Et)CH <sub>2</sub> CO <sub>2</sub> Et	LiN(Pr-i) <sub>2</sub> , THF, -78°C	Ph <sub>3</sub> P=C(CO <sub>2</sub> Et)CHLiCO <sub>2</sub> Et	365
Me <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> Me	LiN(Pr-i) <sub>2</sub> , THF, -78°C	Me <sub>2</sub> NCH <sub>2</sub> CHLiCO <sub>2</sub> Me	366
Me <sub>3</sub> SiCH <sub>2</sub> C(S)OEt	n-BuLi, Et <sub>2</sub> O, -40°C	Me <sub>3</sub> SiCHLiC(S)OEt	367
MeC(O)SH	LiN(Pr-i) <sub>2</sub> , THF, -78°C	LiCH <sub>2</sub> C(O)SLi	368
MeCONMe <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, -78°C	LiCH <sub>2</sub> CONMe <sub>2</sub>	369
MeCH <sub>2</sub> CONMe <sub>2</sub>	Et <sub>2</sub> NLi, HMPA, PhH, -60°C	MeCHLiCONMe <sub>2</sub>	370
MeCONHMe	n-BuLi, THF, 0°C	LiCH <sub>2</sub> CONLiMe	371
Me <sub>3</sub> SiCH <sub>2</sub> CONMe <sub>2</sub>	LiN(Pr-i) <sub>2</sub> or n-BuLi, THF, 0°C	Me <sub>3</sub> SiCHLiCONMe <sub>2</sub>	372
C(O)NHCHPhCH <sub>2</sub>	n-BuLi, THF, 0°C	C(O)NLiCHPhCHLi	373
MeCH(OH)CH <sub>2</sub> CO <sub>2</sub> Et	LiN(Pr-i) <sub>2</sub> , THF, -50°C	MeCH(OLi)CHLiCO <sub>2</sub> Et	374
Me <sub>3</sub> SiCH <sub>2</sub> C(S)NMe <sub>2</sub>	LiN(SiMe <sub>3</sub> ) <sub>2</sub>	Me <sub>3</sub> SiCHLiC(S)NMe <sub>2</sub>	367
MeCH <sub>2</sub> C(S)NHPh	n-BuLi, THF, 0°C	MeCHLiC(S)NLiPh	375
C(S)(CH <sub>2</sub> ) <sub>3</sub> NMe	s-BuLi, THF, -30°C	C(S)CHLi(CH <sub>2</sub> ) <sub>3</sub> NMe	376
MeCOC(=SMe <sub>2</sub> )COMe	n-BuLi, THF, -15°C	LiCH <sub>2</sub> CO(=SMe <sub>2</sub> )COMe	377

TABLE 10. FORMATION OF  $\alpha$ -CYANOSUBSTITUTED ALKYL LITHIUMS VIA LITHIATION

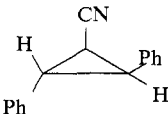
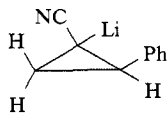
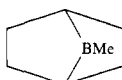
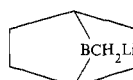
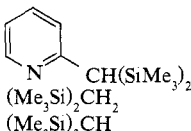
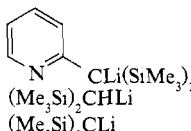
Compound	Lithiating conditions	Product	Refs.
MeCN	n-BuLi, C <sub>6</sub> H <sub>14</sub> , THF, –70°C	LiCH <sub>2</sub> CN	378
EtCH <sub>2</sub> CN	LiNEt <sub>2</sub> , HMPA, PhH, –70°C	EtCHLiCN	379
PhCH <sub>2</sub> CN	n-BuLi, C <sub>5</sub> H <sub>14</sub> , –70°C	PhCHLiCN	380
C <sub>5</sub> H <sub>5</sub> FeC <sub>3</sub> H <sub>4</sub> CH <sub>2</sub> CN	n-BuLi, Et <sub>2</sub> O, RT	h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> FeC <sub>3</sub> H <sub>4</sub> CHLiCN-h <sup>5</sup>	381
Me <sub>3</sub> SiCH <sub>2</sub> CN	n-BuLi or LiNPr-i <sub>2</sub> , Et <sub>2</sub> O, –78°C	Me <sub>3</sub> SiCHLiCN	382
Me <sub>3</sub> SiO(CH <sub>2</sub> ) <sub>2</sub> CN	LiN(Pr-i) <sub>2</sub> , THF, –78°C	Me <sub>3</sub> SiO(CH <sub>2</sub> ) <sub>2</sub> CHLiCN	383
	LiN(Pr-i) <sub>2</sub> , THF, –78°C		384,385

TABLE 11. FORMATION OF  $\alpha$ -METALLO-ALKYL LITHIUMS VIA LITHIATION

Compound	Lithiating conditions	Product	Refs.
Me <sub>3</sub> SiCH <sub>2</sub> BOCMe <sub>2</sub> CMe <sub>2</sub> O	Li·TMP <sup>a</sup> , TMED, THF, 0°C	Me <sub>3</sub> SiCHLiBOCMe <sub>2</sub> CMe <sub>2</sub> O	386
	Li·TMP <sup>a</sup> , PhH, RT		387
CH <sub>2</sub> [BO(CH <sub>2</sub> ) <sub>3</sub> O] <sub>2</sub>	Li·TMP <sup>a</sup> , THF, TMED, –75°C	CLi[BO(CH <sub>2</sub> ) <sub>3</sub> O] <sub>8</sub>	388
	n-BuLi, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , 20°C		389
(Me <sub>3</sub> Si) <sub>2</sub> CH <sub>2</sub>	t-BuLi, THF, HMPA, –78°C	(Me <sub>3</sub> Si) <sub>2</sub> CHLi	390
(Me <sub>3</sub> Si) <sub>3</sub> CH	MeLi, THF, Et <sub>2</sub> O	(Me <sub>3</sub> Si) <sub>3</sub> CLi	391
	t-BuLi-TMED, C <sub>5</sub> H <sub>12</sub>	(Me <sub>3</sub> Si) <sub>2</sub> CHSiMe <sub>2</sub> CH <sub>2</sub> Li	392
(Me <sub>3</sub> Si) <sub>4</sub> C	t-BuLi-TMED, C <sub>5</sub> H <sub>12</sub>	(Me <sub>3</sub> Si) <sub>3</sub> CSiMe <sub>2</sub> CH <sub>2</sub> Li	392
(Ph <sub>3</sub> M) <sub>2</sub> , M = Sn or Pb	LiN(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> , Et <sub>2</sub> O, HMPA, 20°C	(Ph <sub>3</sub> M) <sub>2</sub> CHLi	393
Ph <sub>3</sub> SnCH <sub>2</sub> AsPh <sub>2</sub>	LiN(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> , Et <sub>2</sub> O, HMPA, 20°C	Ph <sub>3</sub> SnCHLiAsPh <sub>2</sub>	393
(Ph <sub>2</sub> M) <sub>2</sub> CH <sub>2</sub> , M = As or Sb	LiN(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> , Et <sub>2</sub> O, HMPA, 20°C	(Ph <sub>2</sub> M) <sub>2</sub> CHLi	393
Ph <sub>2</sub> As(O)Me	LiN(Pr-i) <sub>2</sub> , THF, –40°C	Ph <sub>2</sub> As(O)CH <sub>2</sub> Li	394
Ph <sub>2</sub> As(O)CH <sub>2</sub> Me	LiN(Pr-i) <sub>2</sub> , THF, –40°C	Ph <sub>2</sub> As(O)CHLiMe	395
H <sub>14</sub> (Ph <sub>2</sub> Te) <sub>2</sub> CH <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , –78°C	(PhTe) <sub>2</sub> CHLi	396

<sup>a</sup> Li·TMP = Li tetramethylpiperidine.

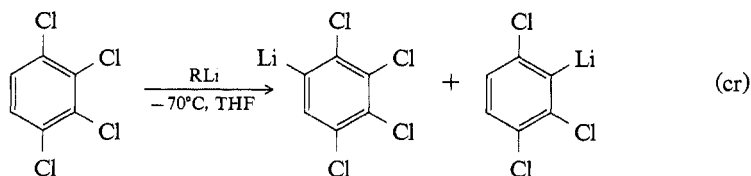
TABLE 12. FORMATION OF LITHIO FORMAMIDES AND THIOFORMAMIDES VIA LITHIATION

Compound	Lithiating conditions	Product	Refs.
HC(O)NMe <sub>2</sub>	LiNPr-i <sub>2</sub> , THF, Et <sub>2</sub> O, -78°C	LiC(O)NMe <sub>2</sub>	397
HC(O)N(Pr-i) <sub>2</sub>	t-BuLi, Et <sub>2</sub> O, THF, C <sub>5</sub> H <sub>12</sub> , -95°C	LiC(O)NPr-i <sub>2</sub>	398
	LiN(Pr-i) <sub>2</sub> , THF, -78°C		399
HC(O)N(CH <sub>2</sub> OMe) <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , THF, -60°C	LiC(O)N(CH <sub>2</sub> OMe) <sub>2</sub>	400
HC(S)NMe <sub>2</sub>	LiN(Pr-i) <sub>2</sub> , C <sub>6</sub> H <sub>14</sub> , THF, -100°C	LiC(S)NMe <sub>2</sub>	401,402

easier with increasing F or Cl substitution, the stability of the lithiated product is also increased, e.g., C<sub>6</sub>Cl<sub>3</sub>Li is stable<sup>512</sup> at +20°C.

For halobenzenes, halogen–Li exchanges and benzyne formation become easier in the sequence I > Br > Cl > F; indeed, for iodides and bromides, the most probable reactions are halogen–lithium exchanges (see §5.5.2.3.3.). Halogenoanisoles, XC<sub>6</sub>H<sub>4</sub>OMe, provide mixtures of products depending on X, the orientation of the two groups and the lithiating conditions<sup>4</sup>.

Metal–halogen exchanges, e.g., of 1,2,3,4-Cl<sub>4</sub>C<sub>6</sub>H<sub>2</sub>, can be suppressed using MeLi or PhLi but not by t-BuLi, e.g.<sup>513</sup>:

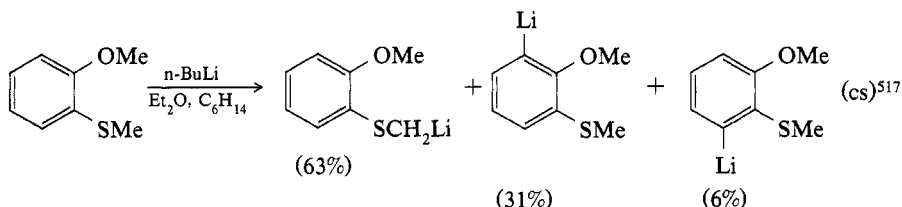


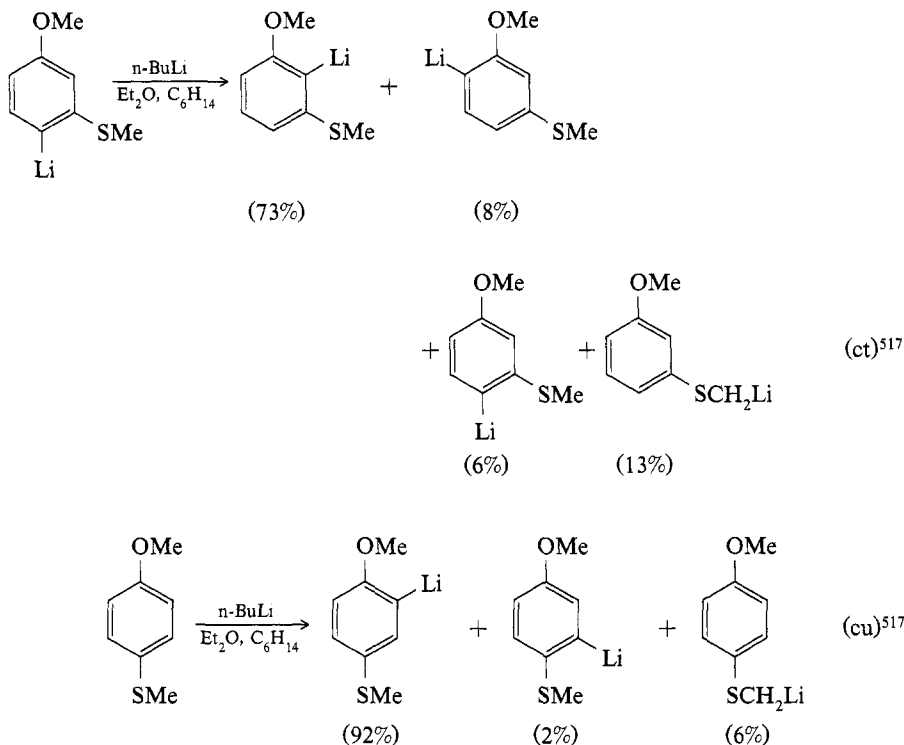
where if R = t-Bu, the product distribution is 0 : 100; if R = Me, it is 93 : 7; if R = Ph, it is 89 : 11. Halogenobenzene, even fluoro compounds, can be alkylated, e.g., 1,3,5-F<sub>3</sub>C<sub>6</sub>H<sub>3</sub> is alkylated<sup>514</sup> by t-BuLi, but is metallated by n-BuLi. Nucleophilic displacement also arises with o-F-<sup>515</sup> and o-MeO-phenyloxazolines<sup>425</sup>.

Aryne formation occurs from di-o-lithiated arylsulfonic acid derivatives<sup>463</sup>.

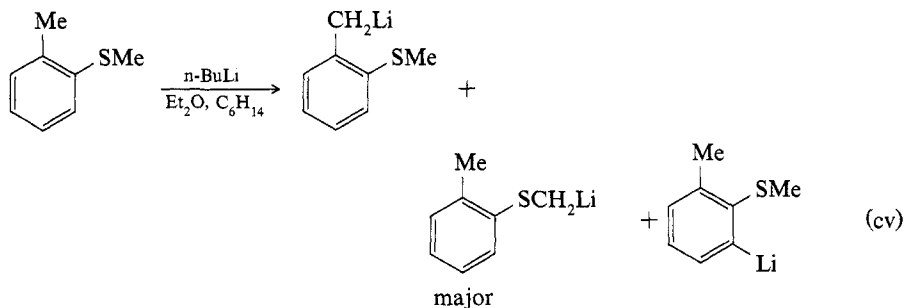
Acidic hydrogens in C–H bonds within the side chain of hetero-substituted benzenes may be metallated, rather than the ring positions. Metallation of benzene derivatives, containing o-methyl groups, e.g., o-XC<sub>6</sub>H<sub>4</sub>Me, X = OR, NR<sub>2</sub>, CONR<sub>2</sub>, SO<sub>2</sub>NR<sub>2</sub>, 2-oxazolinyll or CH<sub>2</sub>NMe<sub>2</sub>, occurs partially (for X = OR or NR<sub>2</sub>) or completely (for the other X groups) at the methyl group [see Eqs. (q)–(r)].

The α protons in thiomethyl groups are acidic; metallation of PhSMe provides<sup>516</sup> the thermodynamic product, PhSCH<sub>2</sub>Li, via the ring-substituted kinetic product, o-LiC<sub>6</sub>H<sub>4</sub>SCH<sub>3</sub>. Even in the presence of OMe groups, small yields of SCH<sub>2</sub>Li can be obtained, e.g.:





Metallation of *o*-MeC<sub>6</sub>H<sub>4</sub>SMe also provides several products, the ratio of which depends on the conditions, e.g.<sup>518</sup>:



The SMe group is, therefore, ortho directing, like SAR groups<sup>519</sup> (cf. Ph<sub>2</sub>S).

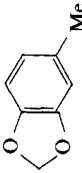
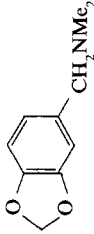
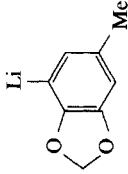
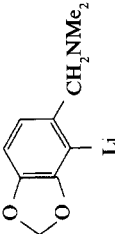
Lithiation of Ph(CH<sub>2</sub>)<sub>n</sub>NMe<sub>2</sub>, *n* = 3, occurs at the benzylic site instead of at an ortho ring site as happens<sup>520</sup> with *n* = 0–2.

For Ph<sub>3</sub>E (E = N<sup>457</sup>, P<sup>457</sup> or As<sup>521</sup>), metallation occurs mainly at the meta position, albeit in low yields.

Of the polycondensed benzenoid compounds, naphthalene itself is metallated by *n*-BuLi in THF in the 1 and 2 positions only in poor yields. Polymetallation occurs using *n*-BuLi·TMED, but *t*-BuLi alkylates naphthalene. Depending on the conditions and

TABLE 13. ORTHO-LITHIATION OF ARENES

Compound	Lithiating conditions	Product	Refs.
PhNMe <sub>2</sub>	n-BuLi, C <sub>6</sub> H <sub>14</sub> , reflux, 16 h	o-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Li	467
PhNC	n-BuLi, C <sub>6</sub> H <sub>14</sub> , TMED, 25°C, 4 h (i) t-BuLi, Et <sub>2</sub> O, -78°C (ii) t-BuLi, TMED	t-Bu(Li)C≡C <sub>6</sub> H <sub>4</sub> Li-o	468
PhN-pyrrole	2 equiv n-BuLi, Et <sub>2</sub> O, TMED, 0°C	o-LiC <sub>6</sub> H <sub>4</sub> NCLi ≡ CHCH ≡ CH	469
PhNHCOBu-t	2 equiv n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , 0°C	o-LiC <sub>6</sub> H <sub>4</sub> NLiCOBu-t	470
PhNHCO <sub>2</sub> Bu-t	2 equiv t-BuLi, C <sub>3</sub> H <sub>12</sub> , THF, -78°C	o-LiC <sub>6</sub> H <sub>4</sub> NLiCO <sub>2</sub> Bu-t	471
PhCH <sub>2</sub> NHMe	2 equiv n-BuLi, Et <sub>2</sub> O, TMED, 5 h	o-MeNLiCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Li	472
PhCH <sub>2</sub> NMe <sub>2</sub>	n-BuLi, Et <sub>2</sub> O, RT	o-Me <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Li	473
PhCHNMeCH <sub>2</sub> CH <sub>2</sub> NMe	n-BuLi, C <sub>6</sub> H <sub>14</sub> , Et <sub>2</sub> O, TMED, 25°C	o-LiC <sub>6</sub> H <sub>4</sub> CHNMe(CH <sub>2</sub> ) <sub>2</sub> NMe	474
PhCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub>	n-BuLi, Et <sub>2</sub> O	o-Me <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Li	475
PhCHOHCH <sub>2</sub> NMe <sub>2</sub>	2 equiv n-BuLi, Et <sub>2</sub> O, 20°C	o-LiC <sub>6</sub> H <sub>4</sub> CHOLiCH <sub>2</sub> NMe <sub>2</sub>	476
PhCONMe <sub>2</sub>	(i) MeLi, THF, -78°C (ii) n-BuLi, C <sub>6</sub> H <sub>14</sub>	o-LiC <sub>6</sub> H <sub>4</sub> C(OLi)MeNMe <sub>2</sub>	477
PhCONEt <sub>2</sub>	s-BuLi-TMED, THF, -78°C	o-LiC <sub>6</sub> H <sub>4</sub> CONEt <sub>2</sub>	478
PhCONHMe	2 equiv n-BuLi, THF, reflux	o-LiC <sub>6</sub> H <sub>4</sub> CONLiMe	479
PhC(S)NHMe	2 equiv n-BuLi, THF, 0°C	o-LiC <sub>6</sub> H <sub>4</sub> C(S)NLiMe	480
PhC ≡ NCM <sub>2</sub> CH <sub>2</sub> O	s-BuLi, Et <sub>2</sub> O, -70°C to 0°C	o-LiC <sub>6</sub> H <sub>4</sub> C ≡ NCM <sub>2</sub> CH <sub>2</sub> O	481
Ph <sub>2</sub> C ≡ NNMe <sub>2</sub>	n-BuLi	o-LiC <sub>6</sub> H <sub>4</sub> (Ph)C ≡ NNMe <sub>2</sub>	482
PhC ≡ NCH <sub>2</sub> CH <sub>2</sub> NH	2 equiv n-BuLi	o-LiC <sub>6</sub> H <sub>4</sub> C ≡ NCH <sub>2</sub> CH <sub>2</sub> NLi	483
PhOMe	n-BuLi, Et <sub>2</sub> O	o-LiC <sub>6</sub> H <sub>4</sub> OMe	484
PhOCONEt <sub>2</sub>	s-BuLi-TMED, THF, -20°C	o-LiC <sub>6</sub> H <sub>4</sub> OCONEt <sub>2</sub>	485
PhOPh	n-BuLi, Et <sub>2</sub> O	o-LiC <sub>6</sub> H <sub>4</sub> OPh	486
PhCH <sub>2</sub> OH	2 equiv n-BuLi, Et <sub>2</sub> O	(o-LiC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> O	487
PhC(CF <sub>3</sub> ) <sub>2</sub> OH	n-BuLi, petroleum ether, TMED, reflux	o-LiC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OLi	488
PhCH(OMe) <sub>2</sub>	2 equiv s-BuLi, cyclo-C <sub>6</sub> H <sub>11</sub> t-BuLi, Et <sub>2</sub> O, -78°C	o-LiC <sub>6</sub> H <sub>4</sub> C(CF <sub>3</sub> ) <sub>2</sub> OLi o-LiC <sub>6</sub> H <sub>4</sub> CH(OMe) <sub>2</sub>	489 490

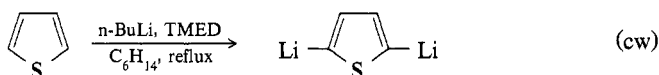
PhSO <sub>3</sub> H	2 equiv n-BuLi, THF, 0°C	491
PhSO <sub>2</sub> NMe <sub>2</sub>	n-BuLi, THF, 0°C	492
PhSO <sub>2</sub> Ph	n-BuLi, Et <sub>2</sub> O, –40°C	493
PhF	4 equiv BuLi, Et <sub>2</sub> O, –30°C	494
Ph <sub>3</sub> P = CH <sub>2</sub>	n-BuLi, THF, –50°C	495
PhCF <sub>3</sub>	s-BuLi, THF, 25°C	496
	n-BuLi, Et <sub>2</sub> O, reflux	484
o-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe		482
o-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	n-BuLi, Et <sub>2</sub> O	497
m-BrC <sub>6</sub> H <sub>4</sub> O <sub>2</sub> SPh	n-BuLi	498
m-MeOC <sub>6</sub> H <sub>4</sub> F	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , –65°C	499
m-CNC <sub>6</sub> H <sub>4</sub> Cl	Li·TMP	482
m-CNC <sub>6</sub> H <sub>4</sub> Cl	n-BuLi, Et <sub>2</sub> O, reflux	484
m-MeOC <sub>6</sub> H <sub>4</sub> CONEt <sub>2</sub>	s-BuLi·TMED, THF, –78°C	478
m-MeOCH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> Me	t-BuLi, petroleum ether, 0°C	500
p-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Me	n-BuLi·TMED, C <sub>6</sub> H <sub>14</sub>	501
p-MeOC <sub>6</sub> H <sub>4</sub> C = NCM <sub>2</sub> CH <sub>2</sub> O	n-BuLi, C <sub>6</sub> H <sub>14</sub> , Et <sub>2</sub> O, –78°C	469
p-FC <sub>6</sub> H <sub>4</sub> Me	n-BuLi, THF	495
p-ClC <sub>6</sub> H <sub>4</sub> OPh	n-BuLi, Et <sub>2</sub> O	486
p-ClC <sub>6</sub> H <sub>4</sub> CONMe <sub>2</sub>	(i) MeLi, THF, –78°C	477
	(ii) n-BuLi, C <sub>6</sub> H <sub>14</sub>	
	n-BuLi, Et <sub>2</sub> O, RT	502
	n-BuLi, Et <sub>2</sub> O, RT	503
		
		
		
		

<sup>a</sup> Li·TMP = Li tetramethylpiperidine

substituents metallation of 1-substituted naphthalenes occurs at the 2- or 8-sites, whereas 2-substituted naphthalenes are metallated at the 1 and/or 3 positions<sup>406</sup>.

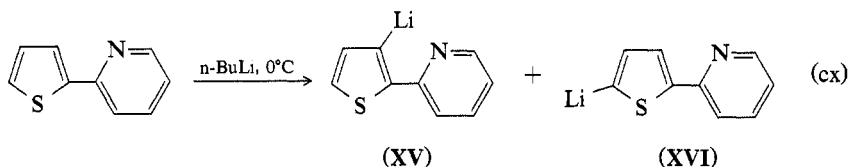
(v) Metallation of Heteroaromatics<sup>9</sup>. For five-membered heterocycles (heteroatom O, N, S, Se or Te) milder conditions can be employed than used for benzenoid derivatives. This allows metallation of five-membered heteroaromatics containing more reactive functional groups, e.g., iodide, than possible for benzenes. The site of lithiation is normally ortho to a ring heteroatom, if free.

a. Thiophenes<sup>522–524</sup>. Thiophene itself is metallated at the 2-position, e.g., by<sup>525</sup> *n*-BuLi in Et<sub>2</sub>O at –35°C or by<sup>406</sup> LiN(Pr-i)<sub>2</sub> in Et<sub>2</sub>O at 0°C and at the 2,5 positions by<sup>522</sup> *n*-BuLi·TMED:

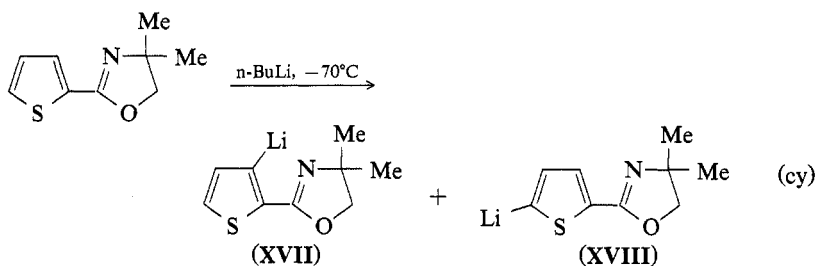


Regarding the site of lithiation of substituted thiophenes:

1. 2-Substituted derivatives are lithiated in the 5-position. Exceptions to this are the pyridyl<sup>526</sup> and 2-oxazolinyl groups<sup>527</sup>; the  $\alpha$ -directing ability of the sulfur in thiophene is superior to other ortho-directing groups, e.g.:

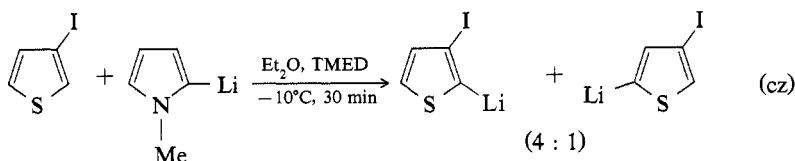


where in THF, (XV):(XVI) = 1:23 and in Et<sub>2</sub>O, (XV):(XVI) = 5:1,



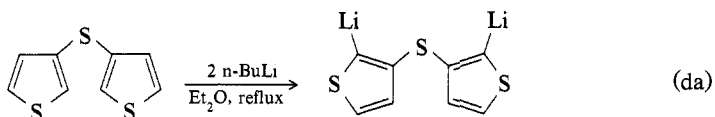
where in THF, XVII:XVIII = 36:55 and in Et<sub>2</sub>O, the XVII:XVIII = 91:4.

2. 3-Substituted derivatives having an ortho-directing ability provide lithiation predominantly in the 2-position; e.g., CH<sub>2</sub>OMe<sup>524</sup>, CO<sub>2</sub>H<sup>527</sup> using LiN(Pr-i)<sub>2</sub> at –70°C), OBu-*t*<sup>528,529</sup>, SMe<sup>530</sup>, SeBu-*n*<sup>531</sup>, CN<sup>532</sup>, Br<sup>533</sup> and I, e.g.<sup>534</sup>:





as well as the other directing groups (see §5.5.2.3.2.iv.), e.g.<sup>535</sup>:

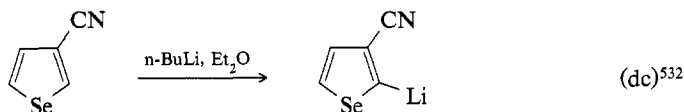
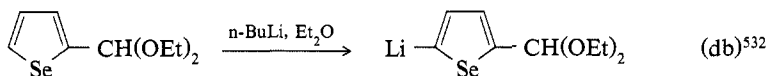


3. 3-Substituted derivatives having no ortho-directing abilities, e.g., alkyl or aryl, are lithiated in the 5-(mainly) and 2-positions depending on the steric hindrance of the substituents<sup>536</sup>.

4. 3,4-Disubstituted and 2,5-disubstituted thiophenes are lithiated ortho to the more powerful group<sup>537</sup>.

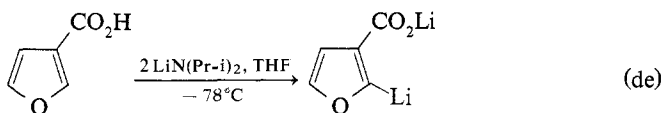
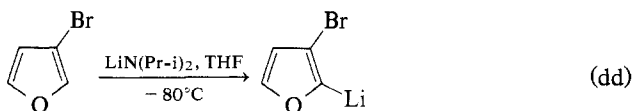
Metallation of benzothiophenes<sup>538</sup> occurs at the  $\alpha$  site and of dibenzothiophenes<sup>539</sup> at the ortho site, if free.

Selenophenes and tellurophenes react similarly to thiophenes, e.g.<sup>406</sup>:

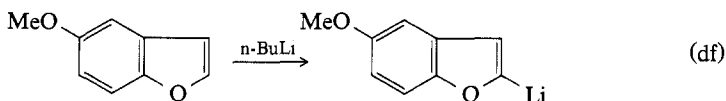


b. Furans. Furan is metallated at the 2-position, e.g., by *n*-BuLi in refluxing  $\text{Et}_2\text{O}$ <sup>540</sup>, but less readily than thiophene. 2,5-Dilithiation results<sup>269</sup> when *n*-BuLi·TMED is used.

2-Substituted furans are metallated at the 5-position; for 2-(2-oxaxolynyl)furan, metallation occurs at the 3- and 5-sites<sup>406</sup>. ortho-Directing groups in the 3-position, including  $\text{Br}$ <sup>541</sup> and  $\text{CO}_2\text{H}$ <sup>542</sup>, direct Li to the 2-site, e.g.:

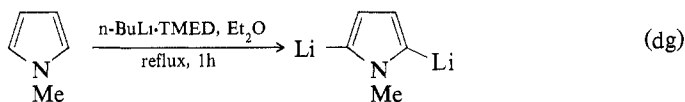


Benzofuran undergoes metallation in the 2-position; even 5-methoxybenzofuran is lithiated at the 2-position<sup>543</sup>:

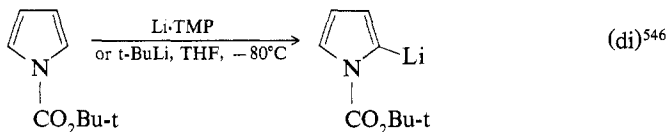
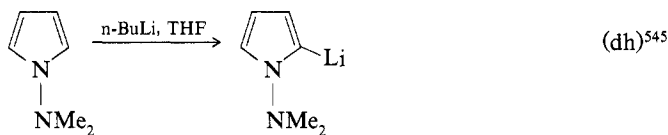


Lithiation of dibenzofuran occurs at the site ortho to the oxygen, if free<sup>539</sup>.

c. Pyrroles. Pyrroles including benzo derivatives are not lithiated as readily as are furans or thiophenes. Pyrrole itself is deprotonated at nitrogen. N-Alkylpyrroles can be lithiated<sup>522</sup> using *n*-BuLi·TMED, Et<sub>2</sub>O at the 2-position and, with xs, at the 2,5-positions, e.g.:



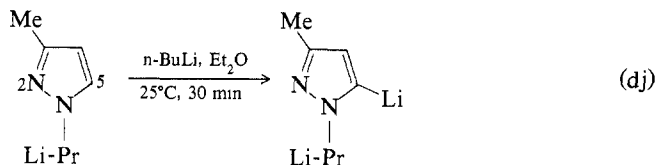
Metallation occurs more readily with N-NMe<sub>2</sub> and N-CO<sub>2</sub>Bu-*t* than with N-Me derivatives of pyrrole:



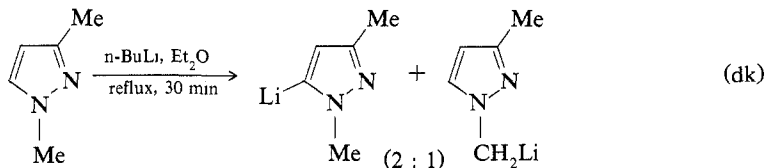
With bulky N-alkylpyrroles, 2,4-dilithiated products can be obtained also<sup>544,547</sup>. N-Aryl pyrroles provide both *o*- and  $\alpha$ -lithiations<sup>548</sup>.

The  $\alpha$ -lithiating abilities<sup>298</sup> of N-CH<sub>2</sub>OMe<sup>549</sup> and N-SO<sub>2</sub>Ph<sup>550</sup> groups in indole are greater than that of N-Me. Unlike the benzofuran derivative [see Eq. (df)], reaction of 5-methoxy-N-methylindole results in lithiation ortho to the OMe group as well as  $\alpha$  to the nitrogen<sup>551</sup>

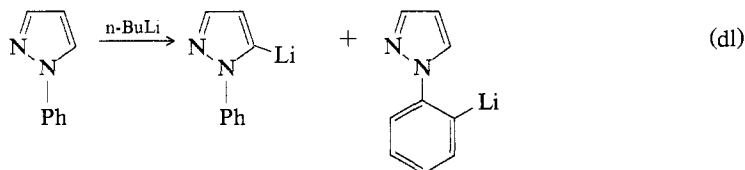
d. Other Five-Membered Heteroaromatics. N-Alkylpyrazoles are metallated in the 5-position, e.g.<sup>552</sup>:



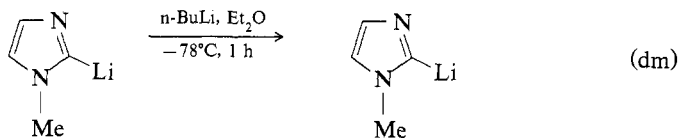
N-Methylpyrazoles also can be metallated at the NMe groups, e.g.<sup>552</sup>:



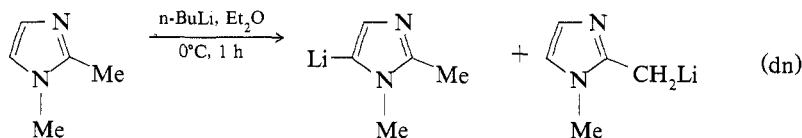
whereas N-phenylpyrazoles can be metallated in the phenyl ring, e.g.<sup>423</sup> [see also Eq. (cn)]:



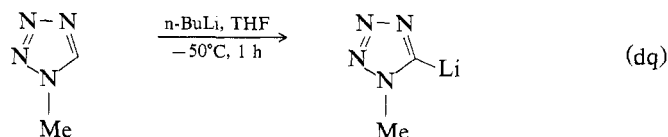
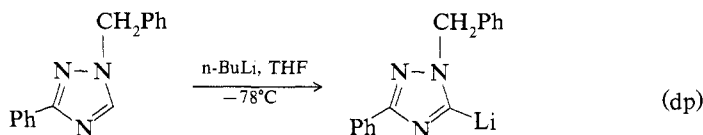
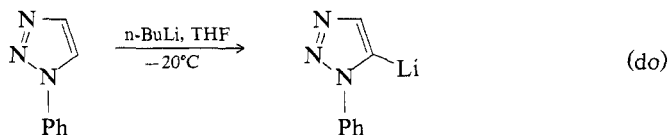
Metallation of imidazoles occurs at the 2-position if free, and if not, at the 5-position, e.g.<sup>553</sup>:



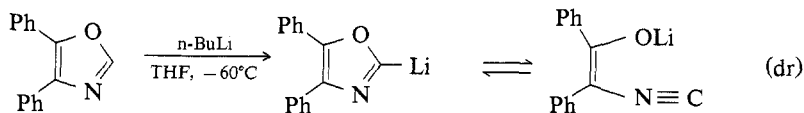
2-Methyl derivatives can be lithiated in the side chain, e.g.<sup>68</sup>:



N-Alkylbenzimidazoles are metallated at the 2-position<sup>554</sup>. 1,2,3-Triazoles<sup>555</sup>, 1,2,4-triazoles<sup>556</sup> and tetrazoles<sup>557</sup> are metallated, e.g.:

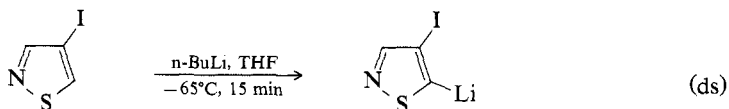


Lithiation of oxazolines proceeds at the 2 site<sup>558</sup>; the ring-substituted product is in equilibrium with an open-chain isomer, e.g.:

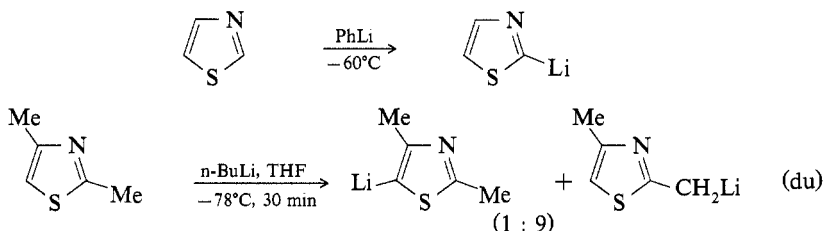


Position 4 is the site of lithiation in 3-Me-5-Ph-isoxazole<sup>559</sup>.

Isothiazoles react<sup>307</sup> at the  $\alpha$  to the sulfur atom; at higher T, fragmentation results. The ease of substitution of isothiazoles enables lithiation even of the 4-iodo derivative<sup>560</sup>:



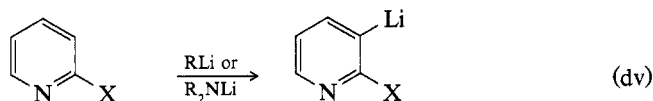
For thiazoles, metallation occurs at the 2-position if free<sup>561</sup> but otherwise at the 5-site<sup>60</sup>. Lithiation of 2-Me derivatives can proceed on the side chain, e.g.<sup>562</sup>:



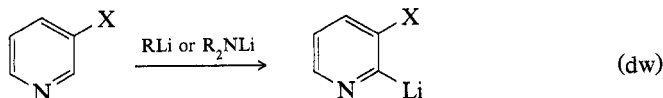
Benzothiazoles react at the 2-position<sup>563</sup>.

e. Pyridines. For 6-membered N-heteroaromatics, 1,2-addition of RLi across the C=N bond (or even 1,4-additions) occur.

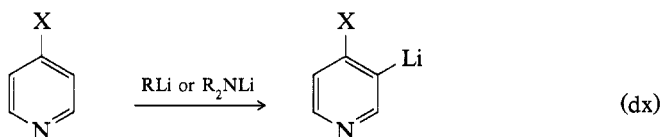
However, in the lithiation of alkoxy-, halo-, amido-, amido- or 2-oxazolinylpyridines, the site of lithiation is ortho to the functional group:



where if X = halide, the reagent is LiN(Pr-i)<sub>2</sub> (THF, -78°C)<sup>564,565</sup>; if X = CON(Pr-i)<sub>2</sub>, the reagent is n-BuLi (THF, -78°C)<sup>566</sup>; if X = CONHCH<sub>3</sub>, the reagent is n-BuLi (THF, -78°C)<sup>567</sup>.

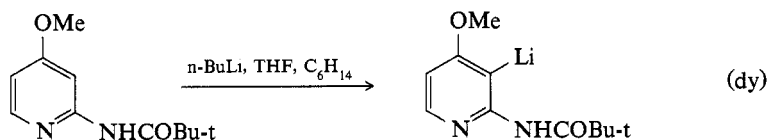


where if X = halide, the reagent is LiN(Pr-i)<sub>2</sub>, (THF, -78°C)<sup>564,568</sup>; if X = CON(Pr-i)<sub>2</sub>, the reagent is n-BuLi (THF, -78°C)<sup>566</sup>; if X = (2-oxazolinyl), the reagent is Li 2,2,6,6-tetramethylpiperidine (TMP)<sup>569</sup>.



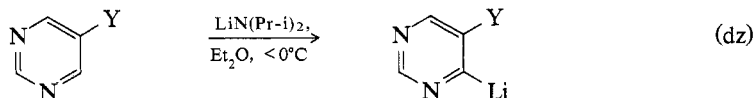
where if X = halide, the reagent is LiN(Pr-i)<sub>2</sub>, (THF, -78°C)<sup>564</sup>; if X = CON(Pr-i)<sub>2</sub>, the reagent is n-BuLi (THF, -78°C)<sup>586</sup>; if X = 2-oxazolinyl, the reagent is MeLi (THF, -78°C)<sup>570</sup>. In contrast to Eq. (ds), the major product from reaction of 3-Cl-pyridine with n-BuLi-TMED in Et<sub>2</sub>O is 2-Li-3-Cl-pyridine<sup>568</sup>.

Another example of ring lithiation is<sup>571</sup>:



Polychloropyridines are more acidic and are more easily metallated<sup>572</sup>, e.g., 2,3,6-Cl<sub>3</sub>C<sub>5</sub>H<sub>2</sub>N (at the 4-position) and 2,3,5,6-Cl<sub>4</sub>C<sub>3</sub>HN by n-BuLi, Et<sub>2</sub>O at -75°C.

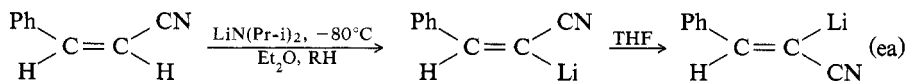
Reactions of *n*-BuLi with halopyridines can lead also to Li-halogen exchange (see §5.5.2.3.3). The reaction between *n*-BuLi and 3-Br-2-Cl-pyridine gives products of Br-Li exchange and metallation of the ring at the 4-position<sup>573</sup>. 5-Methyl<sup>61</sup> and 5-bromopyrimidines<sup>574</sup> also are ring metallated:



where Y = Me or Br.

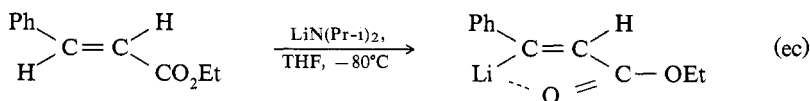
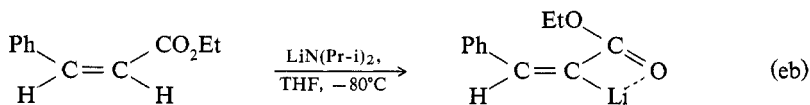
(vi) Metallation of  $\alpha$ -Heterosubstituted Alkenes<sup>9</sup>. Vinyl protons are insufficiently acidic to react with RLi unless the alkene is strained or has hetero substituents. Alpha substituents that allow the replacement of vinylic hydrogens by Li under mild conditions include: RO<sup>575,576</sup>, RS<sup>577-581</sup>, RSe<sup>582,583</sup>, RSO<sup>584-586</sup>, RSO<sub>2</sub><sup>587</sup>, CN<sup>588-591</sup>, CO<sub>2</sub>R<sup>591,592</sup>, CONR<sub>2</sub><sup>591</sup>, NC<sup>593</sup>, NR<sub>2</sub><sup>594,595</sup> and halogens<sup>596,597</sup> (see Table 14).

The metallations under controlled conditions usually proceed with retention of configuration; e.g., (Z)-PhCH=CHCN reacts with LiN(Pr-*i*)<sub>2</sub> in mixed Et<sub>2</sub>O-hydrocarbon (a poorly coordinating medium) at -80°C to provide (Z)-PhCH=CLiCN. However, this undergoes isomerization in the presence of THF or crown ethers to (E)-PhCH=CLiCN:



which also forms<sup>590</sup> directly from (E)-PhCH=CHCN at -113°C using LiN(Pr-*i*)<sub>2</sub>.

Isomers of PhCH=CHCO<sub>2</sub>Et react differently with LiN(Pr-*i*)<sub>2</sub>



The different sites of lithiation of (Z)- and (E)-PhCH=CHCO<sub>2</sub>Et and the configurational stability of the products, even in THF, arise from intramolecular coordination.

Lithiation of 3-(1-pyrrolidinyl)acrylonitrile with LiN(Pr-*i*)<sub>2</sub>, provides the kinetic product below -105°C; at higher T, isomerization to the thermodynamic product occurs<sup>594,595</sup>:

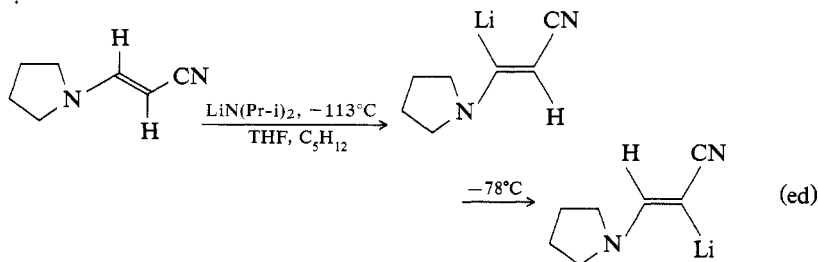


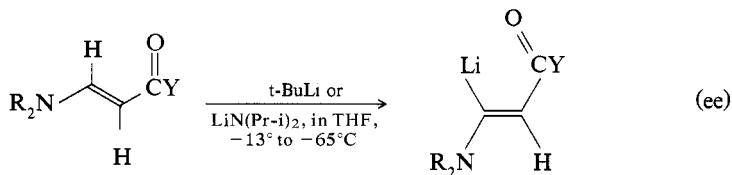


TABLE 14. VINYL LITHIATION OF FUNCTIONALLY SUBSTITUTED ALKENES

Alkene	Lithiating conditions	Product	Refs.
PhCH = CHNC	n-BuLi, THF, Et <sub>2</sub> O, pet. ether, -110°C	(E)-PhCH = CLiNC	598
Ph(OCH <sub>2</sub> OMe)C = CH <sub>2</sub>	s-BuLi, THF, -78°C	(Z)-Ph(OCH <sub>2</sub> OMe)C = CHLi	599
O(CH <sub>2</sub> ) <sub>2</sub> CH = CH	t-BuLi, THF, -78°C	O(CH <sub>2</sub> ) <sub>2</sub> CH = CLi	600
O(CH <sub>2</sub> ) <sub>3</sub> CH = CH	t-BuLi, THF, -78°C	O(CH <sub>2</sub> ) <sub>3</sub> CH = CLi	600
O(CH <sub>2</sub> ) <sub>2</sub> CCl = CH	n-BuLi, THF, -78°C	O(CH <sub>2</sub> ) <sub>2</sub> CCl = CLi	601
CH <sub>2</sub> = CHSeEt	s-BuLi, HMPA, THF, -78°C	CH <sub>2</sub> = CLiSeEt	602
CH <sub>2</sub> = CHTePh	Li-TMP, THF	CH <sub>2</sub> = CLiTePh	603
(Z)-EtSCH = CHSeEt	LiN(Pr-i) <sub>2</sub> , THF, -80°C	(Z)-EtSCH = CHSeEt	604
SCH = CHSC = CSCH = CHS	LiN(Pr-i) <sub>2</sub> , Et <sub>2</sub> O, -70°C	SCH = CHSC = CSCH = CLiS	605
SCH = CHSCH = CH	n-BuLi, C <sub>6</sub> H <sub>14</sub> , THF, -110°C	SCH = CHSCH = CLi	606
(E)-EtOCH = CHSC <sub>3</sub> H <sub>11</sub>	t-BuLi, THF, -70°C	(E)-EtOCH = CLiSC <sub>3</sub> H <sub>11</sub>	607
(E)-PhSCH = CHCO <sub>2</sub> Me	LiN(Pr-i) <sub>2</sub> , THF, C <sub>6</sub> H <sub>14</sub> , -80°C	(E)-PhSCH = CHCO <sub>2</sub> Me	608
o-PyS(O)CH = CHMe	LiN(Pr-i) <sub>2</sub> , THF, -100°C	(Z)-o-PyS(O)CH = CHMe	609
PhSOCH = CHMe	LiN(Pr-i) <sub>2</sub> , THF, -100°C	PhSOCH = CHMe	609
(E)-MeCH = CHSO <sub>2</sub> Ph	MeLi, THF, -95°C	(E)-MeCH = CLiSO <sub>2</sub> Ph	610
CH <sub>2</sub> = CClH	n-BuLi, THF, Et <sub>2</sub> O, pet. ether, -110°C	CH <sub>2</sub> = CCLi	611
(E)-PhCH = CHCl	n-BuLi, THF, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , -80°C	(E)-PhCH = CLiCl	612
(E)-ClCH = CHCl	n-BuLi, THF, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , -100°C	(E)-ClCH = CLiCl	611
(E)-ClCH = CHOEt	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , -100°C	(E)-ClCH = CHOEt	613
(E)-BrCH = CHOEt	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub>	(E)-BrCH = CHOEt	613
CF <sub>2</sub> = CFH	n-BuLi, Et <sub>2</sub> O, -100°C	CF <sub>2</sub> = CFLi	614
CF <sub>2</sub> = CH <sub>2</sub>	s-BuLi, THF, -110°C	CF <sub>2</sub> = CHLi	615
CF <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF = CH	MeLi, Et <sub>2</sub> O, -78°C	CF <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF = CLi	616
	t-BuLi, THF, C <sub>3</sub> H <sub>12</sub> , -45°C		617

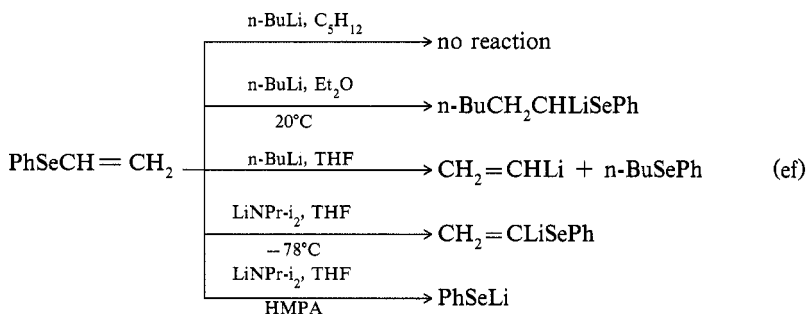
In contrast, lithiation of the ketone, amide or ester analogues provides configurationally stable vinylolithiums<sup>594</sup>:



where if  $\text{R}_2 = \text{---}(\text{CH}_2)_5\text{---}$ ,  $\text{Y} = \text{Ph}$  and if  $\text{R} = \text{---}(\text{CH}_2)_4\text{---}$ ,  $\text{Y} = \text{NEt}_2$  or  $\text{OEt}$ . As well as polarity effects, e.g., dipole stabilization, the stability of the lithiated products is decided by intramolecular complexation and solvation.

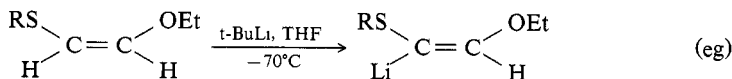
$\alpha$ -Halovinylolithiums are thermally labile (eliminate  $\text{LiY}$ ), and low T is essential for their formation. Substituents, in particular aryl groups, enhance the thermal stability of the  $\alpha$ -halovinylolithiums. Chloro-, fluoro-<sup>618</sup> and bromo-<sup>619,620</sup> alkenes are lithiated.

As well as lithiations, reactions of  $\text{RSCH}=\text{CH}_2$  with  $\text{RLi}$  may result in additions which can be prevented by the use of low T, and  $\text{LiNR}_2$  instead of  $\text{RLi}$ . Vinylselenides react with lithiating agents, e.g.<sup>582,583</sup>:



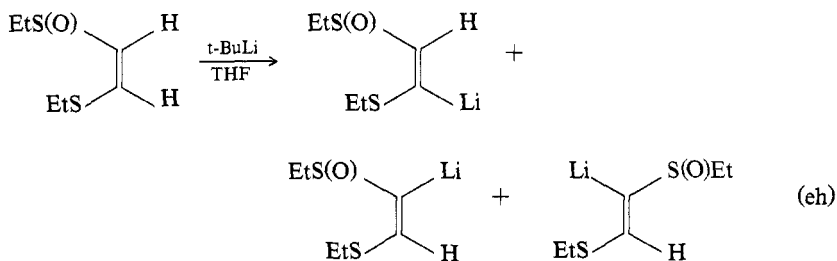
Therefore, deprotonations are brought about by  $\text{LiNR}_2$ , and  $\text{PhSeCH}=\text{CH}_2$  is more readily deprotonated by  $\text{LiN(Pr-}i\text{)}_2$  in THF at  $-78^\circ \text{C}$  than is  $\text{PhSCH}=\text{CH}_2$  (the Se compound is also thermodynamically the more acidic)<sup>583</sup>. Selenophene is also more acidic than thiophene: cf. findings for other S and Se compounds, e.g.,  $\text{PhYCH}_2\text{CH}=\text{CH}_2$  and  $\text{ArYMe}$  ( $\text{Y} = \text{S}$  or  $\text{Se}$ ), in which the sulfur derivatives are the more readily deprotonated<sup>583</sup>. The  $m\text{-CF}_3\text{C}_6\text{H}_4\text{Se}$  group enhances the acidity of  $\alpha$ -hydrogens relative to the  $\text{PhSe}$  group<sup>583</sup>.

Lithiation of  $(Z)\text{-RSCH}=\text{CHOEt}$  occurs  $\alpha$  to the RS group, indicating the superiority of RS over RO groups as  $\alpha$ -directing groups:



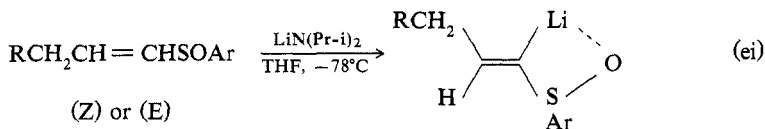
where  $\text{R} = \text{Ph}$  or  $\text{C}_5\text{H}_{11}$ . Some isomerization subsequently occurs<sup>581</sup>. Greater configurational instability is shown<sup>595</sup> by  $(Z)\text{-EtSCH}=\text{CLiCN}$ . It isomerizes even at  $-113^\circ \text{C}$  when prepared from  $(Z)\text{-EtSCH}=\text{CHCN}$  and  $\text{t-BuLi}$  in THF; i.e., lithiation occurs  $\alpha$  to CN even in the presence of SR. Side products in the reactions of  $(Z)\text{-RSCH}=\text{CHSR}$  with lithiating agents are alkynes,  $\text{HC}\equiv\text{CSR}$ , formed<sup>580</sup> by elimination

of LiSR from the initial product, (Z)-RSCH=CLiSR. The products of reaction of (Z)-EtS(O)CH=CHSEt with *t*-BuLi in THF are T-dependent<sup>595</sup>:

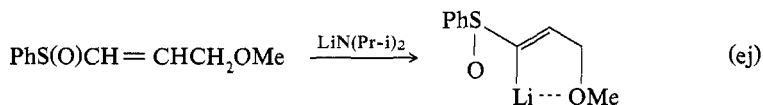


T(°C)	Ratio of Products
-120	5:75:10
-100	31:59:10
-80	73:17:10

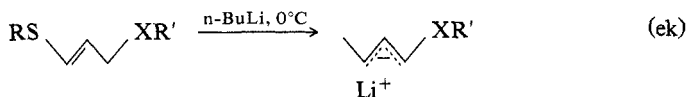
Both (Z)- and (E)-1-alkenylsulfoxides provide exclusively the (E)-vinyl lithium products<sup>586</sup> even at  $-78^\circ\text{C}$ :



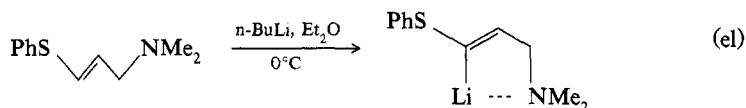
where  $\text{R} = \text{C}_5\text{H}_{11}$ ,  $\text{C}_8\text{H}_{17}$ ;  $\text{Ar} = \text{Ph}$  or  $p\text{-MeC}_6\text{H}_4$ . The SO group lowers the alkene isomerization barrier. It is also a powerful  $\alpha$ -directing group and even directs lithiation into the alkenyl site rather than the allyl site in  $\text{RCH}_2\text{CH}=\text{CHSOAr}$ , e.g.<sup>584</sup>:



Metallation of the sulfide analogues, (E)-RSCH=CHCH<sub>2</sub>XR' ( $\text{X} = \text{S}$  or  $\text{O}$ ) occurs at the  $\text{sp}^3$  carbon, i.e., the allylic position:



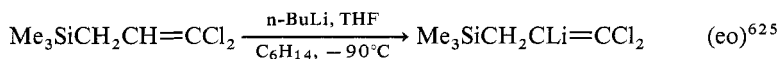
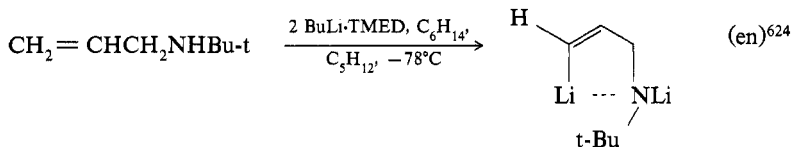
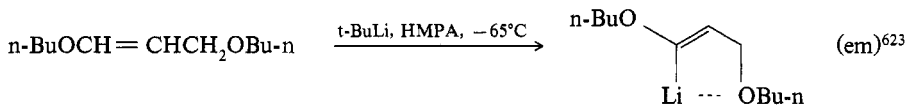
where  $\text{R}, \text{R}', \text{X} = \text{Me}, \text{Me}, \text{S}$ <sup>348</sup>;  $\text{R}, \text{R}', \text{X} = \text{Ph}, \text{Me}, \text{O}$ <sup>349</sup>; but for (E)-PhSCH=CHCH<sub>2</sub>NMe<sub>2</sub> reaction is at the vinylic site<sup>621</sup>:





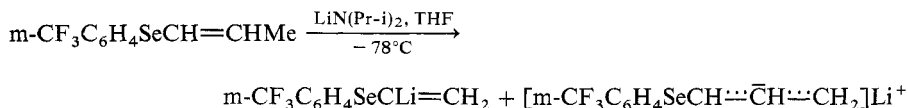
The differences arise from the N being less electronegative than O or S (and hence being less of an  $\alpha$ -directing group), and from the amine both depolymerizing the *n*-BuLi aggregate (thereby making *n*-BuLi more reactive) and acting as an internal donor site.

Even in the presence of allylic protons, vinyl deprotonation occurs in:



However, additions to the double bonds occur instead in<sup>624</sup>  $\text{PhCH=CHCH}_2\text{NHBu-t}$  and in<sup>626</sup>  $\text{CH}_2=\text{CHCH}_2\text{OH}$ .

Both vinyl and allylic protons in  $\text{ArSeCH=CHMe}$  (Z or E) (Ar = *m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub> or Ph) are replaced by Li using  $\text{LiN(Pr-}i)_2$  at  $-78^\circ\text{C}$  in THF to give  $\text{ArSeCHLi=CHMe}$  and  $[\text{ArSeCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2]\text{Li}^+$ , respectively<sup>583</sup>. The vinylic products isomerize to the allylic products and the latter comprise the major components, e.g.:



Time (h)	Product ratio (%)
1	30:58
5	20:70

The acidity of  $\text{ArSeCH=CHR}$  (R = Et or Pr-*i*) is lower than that of  $\text{ArSeCH=CHMe}$ , and deprotonations require more powerful conditions, e.g.,  $\text{Li} \cdot \text{TMP}$  (1–5 equiv) in THF at  $-50^\circ\text{C}$  for  $\text{m-CF}_3\text{C}_6\text{H}_4\text{SeCH=CHR}$ . Reactions occur solely at the vinylic sites to give the same isomeric mixture of  $\text{ArSeCLi=CHR}$  from either the (Z) or the (E) isomer. Deprotonations of  $\text{ArSeCH=CMe}_2$  are carried out successfully using  $\text{LiN(Pr-}i)_2$  or  $\text{Li} \cdot \text{TMP}$  in THF at  $-78^\circ$ , to  $-50^\circ\text{C}$ ; in these cases only allyllithiums,  $[\text{ArSeCH} \cdots \bar{\text{C}}\text{Me} \cdots \text{CH}_2]\text{Li}^+$ , are obtained. The sulfides,  $\text{ArSCH=CHR}$  (R = Et or Pr-*i*), give vinylolithiums exclusively. Competitive allyl and vinyl metallations are known for 1-propenylsulfides and ethers.

(vii) Hetero-Substituted Allylic, Propargylic and Allenic Lithiums<sup>627</sup>. As indicated in §5.5.2.3.2.i, allylic, propargylic and allenic hydrogens are sufficiently reactive to be substituted by Li using either  $\text{RLi}$  or  $\text{R}_2\text{NLi}$ . The presence of  $\alpha$ -hetero-substituted groups enhances the acidity. Tables 15 and 16 list some examples.

TABLE 15. FORMATION OF FUNCTIONALLY SUBSTITUTED ALLYLLITHIUMS VIA LITHIATION

Compound	Lithiating conditions	Product	Refs.
$\text{N}(\text{CH}_2)_3\text{CH}_2\text{CH}=\text{CH}_2$	s-BuLi, THF, $-78^\circ\text{C}$ to $-10^\circ\text{C}$	$[\text{N}(\text{CH}_2)_3\text{CH}_2\text{CH}=\text{CH}]\text{Li}^+$	628
$\text{CH}_2=\text{CHCH}_2\text{NC}$	n-BuLi, THF, $-70^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	629
$\text{CH}_2=\text{CHCH}_2\text{NHCOCu-t}$	2 equiv LiN(Pr- $i$ ) $_2$ , diglyme, $-78^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	630
$\text{CH}_2=\text{CHCH}_2\text{NO}_2$	n-BuLi, THF, HMPA, $-80^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	631
$\text{CH}_2=\text{CHCH}_2\text{NMe}(\text{NO})$	LiN(Pr- $i$ ) $_2$ , THF, $-78^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	632
$\text{CH}_2=\text{CHCH}_2\text{NMeP}(\text{O})(\text{NMe})_2$	n-BuLi, THF, $-50^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	633
$\text{CH}_3\text{CH}=\text{C}(\text{NMePh})\text{CN}$	LiN(Pr- $i$ ) $_2$ , THF, $\text{C}_6\text{H}_{14}$ , $-78^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	634
t-BuNCH $_2$ C = CH $_2$	n-BuLi, TMED, $-78^\circ\text{C}$	$[\text{t-BuNCH}=\text{C}]\text{Li}^+$	635
cis-MeCH = CHCH $_2$ P(O)Ph $_2$	n-BuLi, THF, $-70^\circ\text{C}$	$[\text{MeCH}=\text{CH}]\text{Li}^+$	636
CH $_2$ P(O)PhCH $_2$ CMe = CMe	n-BuLi, THF, $-75^\circ\text{C}$	$[\text{CH}_2\text{P}(\text{O})\text{PhCH}=\text{CMe}]\text{Li}^+$	637
CH $_2$ P(S)PhCH $_2$ CMe = CMe	t-BuLi, THF, $-70^\circ\text{C}$	$[\text{CH}_2\text{P}(\text{S})\text{PhCH}=\text{CMe}]\text{Li}^+$	638
CH $_2$ P(O)OEtCH $_2$ CMe = CMe	n-BuLi, THF, $-75^\circ\text{C}$	$[\text{CH}_2\text{P}(\text{O})\text{OEtCH}=\text{CMe}]\text{Li}^+$	637
CH $_2$ P(S)OEtCH $_2$ CMe = CMe $_2$	n-BuLi, THF, TMED, $-75^\circ\text{C}$	$[\text{CH}_2\text{P}(\text{S})\text{OEtCH}=\text{CMe}]\text{Li}^+$	639
CH $_2$ = CHCH $_2$ P(O)(NMe) $_2$	n-BuLi, THF, $-78^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	640
MeCH = CHCH $_2$ P(O)(OEt) $_2$	n-BuLi, THF, $-60^\circ\text{C}$	$[\text{MeCH}=\text{CH}]\text{Li}^+$	641
CH $_2$ = CHCH $_2$ OP(O)(OEt) $_2$	n-BuLi, THF, $-70^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	642
CH $_2$ = CHCH $_2$ OP(O)(NMe) $_2$	n-BuLi, THF, $-70^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	642
CH $_2$ = CHCH $_2$ OMe	s-BuLi, THF, $-65^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	643-645
CH $_2$ = CHCH $_2$ OSiMe $_3$	t-BuLi, THF, $-78^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	646
CH $_2$ = CHCH(OR) $_2$	s-BuLi, THF, Et $_2$ O, C $_5$ H $_{12}$ , $-95^\circ\text{C}$	$[\text{CH}_2=\text{CH}]\text{Li}^+$	647
CH $_2$ OCMe $_2$ OCH $_2$ C = CH $_2$	s-BuLi, THF, $-78^\circ\text{C}$	$[\text{CH}_2\text{OCMe}_2\text{OCH}=\text{C}]\text{Li}^+$	648
Ph $_2$ P(O)CHOMeCH = CH $_2$	LiN(Pr- $i$ ) $_2$ , THF, $-70^\circ\text{C}$	$[\text{Ph}_2\text{P}(\text{O})\text{C}(\text{OMe})=\text{CH}]\text{Li}^+$	649
Me $_3$ SiCH = CHCH[POEt] $_2$ OP(O)(OEt) $_2$	t-BuLi, THF, C $_6$ H $_{14}$ , $-78^\circ\text{C}$	$[\text{Me}_3\text{SiCH}=\text{CH}]\text{Li}^+$	650
MeCH = CHCH(CN)OSiMe $_3$	LiN(Pr- $i$ ) $_2$ , THF, $-78^\circ\text{C}$	$[\text{MeCH}=\text{CH}]\text{Li}^+$	651,652

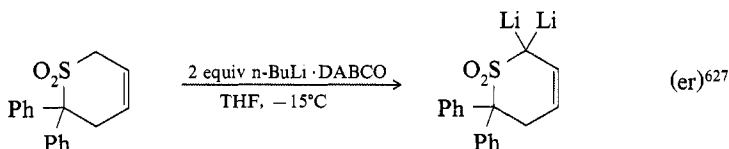
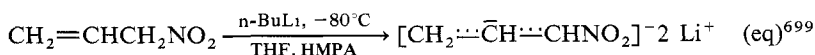
$\text{CH}_2 = \text{CHCH}_2\text{SH}$	2 equiv n-BuLi-TMED, THF, $\text{C}_6\text{H}_4$ , $0^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHSLiLi}]^+$	653
$\text{Me}_2\text{C} = \text{CHCH}_2\text{SPh}$	n-BuLi, THF, $-70^\circ\text{C}$	$[\text{Me}_2\text{C} \cdots \bar{\text{C}}\text{H} \cdots \text{CHSPHLi}]^+$	654
$\text{CH}_2 = \text{CHCH}_2\text{SCH}_2\text{CO}_2\text{Me}$	(i) LiN(Pr- <i>i</i> ) <sub>2</sub>	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHSCHLiCO}_2\text{Me}]^+\text{Li}^+$	655
	(ii) s-BuLi, THF, $-78^\circ\text{C}$	$[\text{o-pySCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2\text{Li}]^+$	656
$\text{o-pySCH}_2\text{CH}=\text{CH}_2$	n-BuLi, THF, $-30^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHSCH} \cdots \text{CH} \cdots \text{CH}_2\text{Li}]^+$	657
$\{\text{CH}_2 = \text{CHCH}_2\}_2\text{S}$	n-BuLi-TMED, THF, $-78^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHSCH} \cdots \text{CH}_2\text{Li}]^+$	658
$\text{MeSCH} = \text{CHCH}_2\text{SMe}$	s-BuLi, THF, $-78^\circ\text{C}$	$[\text{MeSCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CHSMeLi}]^+$	659
$\text{MeSCH}_2\text{CH} = \text{CHCO}_2\text{Me}$	s-BuLi, Et <sub>2</sub> O, $-78^\circ\text{C}$	$[\text{MeSCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CHCO}_2\text{Me}]^+\text{Li}^+$	660
$\text{PhCOCMe} = \text{C(SMe)}_2$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$	$[\text{H}_2\text{C} \cdots \bar{\text{C}}(\text{OPh}) \cdots \text{C(SMe)}_2\text{Li}]^+$	661
	LiN(Pr- <i>i</i> ) <sub>2</sub>	$[\text{S(CH}_2)_3\text{SCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2\text{Li}]^+$	662
$\text{S(CH}_2)_3\text{SCH}=\text{CH}_2$	n-BuLi, THF, $-78^\circ\text{C}$ to $0^\circ\text{C}$	$[\text{S(CH}_2)_3\text{SC} \cdots \text{C} \cdots \text{CH(CH}_2)_2\text{CH}_2\text{Li}]^+$	663
$\text{S(CH}_2)_3\text{SC} = \text{C(CH}_2)_3\text{CH}_2$	n-BuLi, THF, HMPA	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHSOPhLi}]^+$	664
$\text{CH}_2 = \text{CHCH}_2\text{SOPh}$	n-BuLi, THF, $-50^\circ\text{C}$	$[\text{CH}_2\text{CH}_2\text{CH} \cdots \bar{\text{C}}\text{H} \cdots \text{HSOPhLi}]^+$	665
$\text{CH}_2\text{CH}_2\text{CH} = \text{CHCHSOPh}$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-60^\circ\text{C}$	$[\text{H}_2\text{C} \cdots \bar{\text{C}}\text{H} \cdots \text{CHSO}_2\text{PhLi}]^+$	666
$\text{H}_2\text{C} = \text{CHCH}_2\text{SO}_2\text{Ph}$	n-BuLi, HMPA, THF, $-78^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{Me} \cdots \text{CHSO}_2\text{C}_6\text{H}_4\text{Me-p}]^+\text{Li}^+$	667
$\text{CH}_2 = \text{CMeCH}_2\text{SO}_2\text{C}_6\text{H}_4\text{Me-p}$	MeLi, THF, $-20^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{Me} \cdots \text{CHSCSCH}_2\text{Li}]^+\text{Li}^+$	668
$\text{CH}_2 = \text{CMeCH}_2\text{SC(S)Me}$	2 equiv n-BuLi, THF, $-78^\circ\text{C}$	$[\text{MeCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CHSCO(NMe)}_2\text{Li}]^+$	669
$\text{MeCH} = \text{CHCH}_2\text{SC(O)NMe}_2$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CH SC(S)NMe}_2\text{Li}]^+$	670,671
$\text{CH}_2 = \text{CHCH}_2\text{SC(S)NMe}_2$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF	$[\text{CH}_2 \cdots \bar{\text{C}}(\text{OMe}) \cdots \text{CHSCSNMe}_2\text{Li}]^+$	672
$\text{CH}_2 = \text{C(OMe)CH}_2\text{SC(S)NMe}_2$	LiN(Pr- <i>i</i> ) <sub>2</sub>	$[\text{PhSeCH} \cdots \bar{\text{C}}\text{H} \cdots \text{CH}_2\text{Li}]^+$	673
$\text{PhSeCH}_2\text{CH} = \text{CH}_2$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$	$[\text{PhSeCH} \cdots \bar{\text{C}}\text{Me} \cdots \text{CH}_2\text{Li}]^+$	674
$\text{PhSeCH} = \text{CMe}$	Li-TMP <sup>a</sup> m THF, $-78^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CC}_2\text{Li}]^+$	675
$\text{CH}_2 = \text{CHCHCl}_2$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHClLi}]^+$	676
$\text{CH}_2 = \text{CHCH}_2\text{Cl}$	LiN(Pr- <i>i</i> ) <sub>2</sub> , THF, $-78^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{H} \cdots \text{CHCNLi}]^+$	677
$\text{CH}_2 = \text{CHCH}_2\text{CN}$	MeLi, Et <sub>2</sub> O, THF, $-100^\circ\text{C}$	$[\text{CH}_2 \cdots \bar{\text{C}}\text{Bu-n} \cdots \text{CHCO}_2\text{Li}]^+\text{Li}^+$	678
n-BuMeC = CHCO <sub>2</sub> H	LiN(Pr- <i>i</i> ) <sub>2</sub>	$\text{CH}_2 = \text{C(CH}_2\text{Li)CONLiBu-t}$	679
$\text{CH}_2 = \text{CMeCONHtBu-t}$	2 equiv n-BuLi-TMED, THF, $-70^\circ\text{C}$ to $-20^\circ\text{C}$	$\text{CH}_2 = \text{C(CH}_2\text{Li)CH}_2\text{NMe}_2$	680
$\text{CH}_2 = \text{CMeCH}_2\text{NMe}_2$	n-BuLi-TMED, THF, $0^\circ\text{C}$		

<sup>a</sup> Li-TMP = Li tetramethylpiperidine

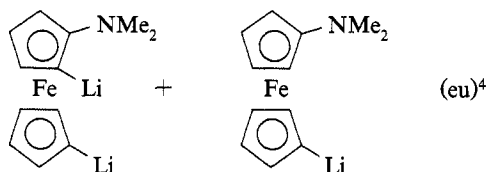
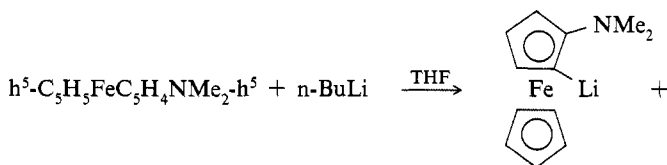
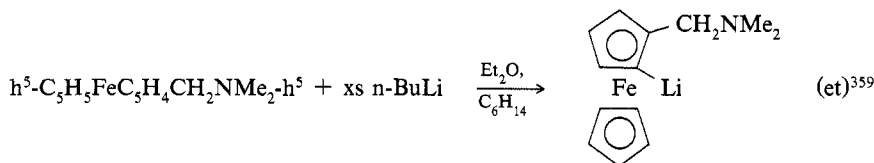
TABLE 16. FORMATION OF FUNCTIONALLY SUBSTITUTED ALKYNYL-, PROPARGYL-,  
 ALLENYL- AND OTHER ALKENYL LITHIUMS VIA LITHIATION

Compound	Lithiating conditions	Product	Refs.
$\text{HC} \equiv \text{CCO}_2\text{H}$	$\text{LiN}(\text{Pr}-i)_2$ , HMPA, THF, $-45^\circ\text{C}$	$\text{LiC} \equiv \text{CCO}_2\text{Li}$	681
$\text{CH}_3\text{C} \equiv \text{CCO}_2\text{H}$	$\text{LiN}(\text{Pr}-i)_2$ , or $n\text{-BuLi}$ :TMED	$\text{LiCH}_2\text{C} \equiv \text{CCO}_2\text{Li}$	682
$\text{Me}_3\text{SiC} \equiv \text{CCH}_3$	$n\text{-BuLi}$ :TMED, $\text{Et}_2\text{O}$ , $-15^\circ\text{C}$	$\text{LiCH}_2\text{C} \equiv \text{CSiMe}_3$	683
$\text{C}_3\text{H}_{11}\text{C} \equiv \text{CCH}_2\text{OMe}$	$n\text{-BuLi}$ :TMED	$\text{LiC}_3\text{H}_{11}\text{C} \equiv \text{C} = \text{CHOMe}$	684
$\text{CH}_2 = \text{C} = \text{CHOMe}$	$n\text{-BuLi}$ , $\text{Et}_2\text{O}$ , $-25^\circ\text{C}$	$\text{CH}_2 = \text{C} = \text{CLiOMe}$	685
$\text{CH}_2 = \text{C} = \text{O}(\text{OMe})\text{Bu-n}$	$n\text{-BuLi}$	$\text{LiCH} = \text{C} = \text{CBu-n}(\text{OMe})$	686
$\text{MeSC} \equiv \text{CCH}_2\text{OMe}$	$\text{LiN}(\text{Pr}-i)_2$ , THF, $-60^\circ\text{C}$	$\text{MeSCLi} = \text{C} = \text{CHOMe}$	687
$\text{MeSCH}_2\text{C} \equiv \text{CCH}_2\text{SMe}$	2 equiv $n\text{-BuLi}$ , $\text{Et}_2\text{O}$ , $-50^\circ\text{C}$	$\text{MeSCHLiC} \equiv \text{CCHLiSMe}$	688
$\text{MeSC(Me)C} = \text{C} = \text{CHOMe}$	$\text{LiNEt}_2$ , THF, $-60^\circ\text{C}$	$\text{MeSC(Me)C} = \text{C} = \text{CLiOMe}$	687
$\text{EtC} \equiv \text{CCH}(\text{SEt})_2$	$n\text{-BuLi}$ , $\text{Et}_2\text{O}$ , $-33^\circ\text{C}$	$\text{EtC} \equiv \text{CCLi}(\text{SEt})_2$	689
$\text{HC} = \text{CCH}_2\text{SPh}$	$n\text{-BuLi}$	$\text{LiC} \equiv \text{CCHLiSPh}$	690
$\text{HC} \equiv \text{CCH}_2\text{SePh}$	$\text{LiN}(\text{Pr}-i)_2$ , THF, $-78^\circ\text{C}$	$\text{LiC} \equiv \text{CCHLiSePh}$	691
$\text{MeC} \equiv \text{CNEt}$	$n\text{-BuLi}$ :TMED, $\text{Et}_2\text{O}$ , $0^\circ\text{C}$	$\text{LiCH}_2\text{C} \equiv \text{CNEt}_2$	692
$\text{C}_6\text{H}_{11}\text{C} \equiv \text{CCH}_2\text{NMe}_2$	$n\text{-BuLi}$ , THF, $-70^\circ\text{C}$	$\text{C}_6\text{H}_{11}\text{C} \equiv \text{CCHLiNMe}_2$	693
$\text{CH}_2 = \text{C} = \text{CHNMeP}(\text{O})(\text{OEt})_2$	$n\text{-BuLi}$ , THF	$\text{CH}_2 = \text{C} = \text{CLiNMeP}(\text{O})(\text{OEt})_2$	694
$\text{MeOC} = \text{CHCH}_2\text{CH} = \text{C}(\text{OMe})\text{CH}_2$	$t\text{-BuLi}$ , THF, $-78^\circ\text{C}$	$\text{MeOC} = \text{CHCH}_2\text{CH} = \text{C}(\text{OMe})\text{CHLi}$	695
$\text{CH}_2 = \text{CHCH} = \text{CHOMe}$	$t\text{-BuLi}$ , THF, $-78^\circ\text{C}$	$\text{CH}_2 = \text{CHCH} = \text{C}(\text{OMe})\text{Li}$	696
$\text{PhCH} = \text{CHCMe} = \text{CHCl}$	$n\text{-BuLi}$ , THF, $\text{C}_6\text{H}_{14}$ , $-70^\circ\text{C}$	$\text{PhCH} = \text{CHCMe} = \text{CLiCl}$	697
$\text{Me}_2\text{C} = \text{CHCH} = \text{NBu-t}$	$\text{LiNPr}-i_2$ , $\text{Et}_2\text{O}$	$[\text{CH}_2 \cdots \text{CMe} \cdots \text{CH} \cdots \text{CH} \cdots \text{NBu-t}]\text{Li}^+$	698

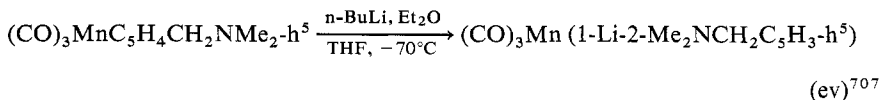
As well as monoanions, dianionic compounds can be obtained, e.g.:



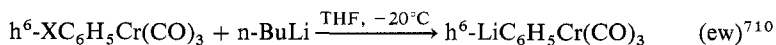
(viii) Transition-Metal Complexes. Ferrocene is metallated<sup>3,4,406,701</sup> by *n*-BuLi in Et<sub>2</sub>O to give monolithio and 1,1'-dilithio derivatives; the addition of TMED allows formation of quantitative yields of (h<sup>5</sup>-LiC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe. Further metallation using *xs* *n*-BuLi can provide compounds incorporating<sup>4</sup> up to seven Li atoms. Metallation of substituted ferrocenes follows the same pattern described for substituted benzenes; ferrocenes are metallated more readily than their benzene analogues. Ortho-metallation (to Cl) of h<sup>5</sup>-ClC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>-h<sup>5</sup> occurs<sup>702</sup>. Heteroannular dimetallation can result, e.g.<sup>703</sup>:



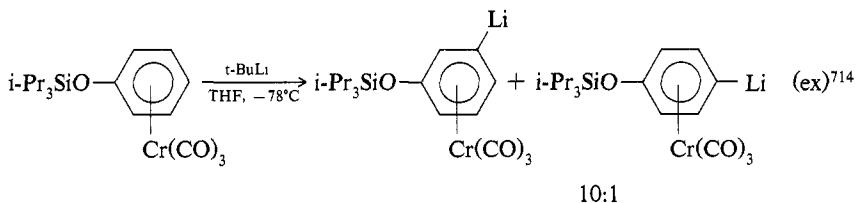
Lithiations of ruthenocene<sup>704</sup> and osmocene<sup>705</sup> as well as h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub> (M = Mn<sup>705</sup> and Re<sup>706</sup>) derivatives react similarly, e.g.:



Dibenzenechromium is lithiated more readily than PhH; polyolithiation can result<sup>708,709</sup>. Arene-Cr(CO)<sub>3</sub> compounds, h<sup>6</sup>-XC<sub>6</sub>H<sub>5</sub>Cr(CO)<sub>3</sub> (X = H, OMe, F, Cl)<sup>710-712</sup>, are metallated by n-BuLi, e.g.:



In contrast to lithiation of 3-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH (at site 2), lithiation of (h<sup>6</sup>-3-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH)Cr(CO)<sub>3</sub> occurs at the 4-position<sup>713</sup>. meta-Lithiations of i-Pr<sub>3</sub>SiO- and MeSi(Pr-i)<sub>3</sub> N-substituted (arene)Cr(CO)<sub>3</sub> complexes are known<sup>714,715</sup> e.g.:



(J. L. WARDELL)

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#### 5.5.2.3.3. by Halogen–Lithium Exchange with Organic Halides.<sup>1,2</sup>

The halogen–Li exchange:



is reversible, and equilibrium constants are known<sup>3,4</sup>, e.g., values for interaction of RLi and PhI:



where

$$K = \frac{[\text{PhLi}][\text{RI}]}{[\text{PhI}][\text{RLi}]} \quad (\text{c})$$

at  $-70^\circ\text{C}$  in  $\text{Et}_2\text{O}$  [ $\text{R}(\log K) = \text{CH}_2=\text{CH}$  (–2.41), cyclo- $\text{C}_3\text{H}_5$  (0.98), Et (3.5), n-Pr (3.9), t-Bu $\text{CH}_2$  (6.1), cyclo- $\text{C}_5\text{H}_9$  (6.9)].

The values of  $K$  are similar in ether and in ether–pentane<sup>3</sup>. The different extents of aggregation also have little impact on  $K$ .

Values are also calculated for exchanges<sup>4</sup> involving aryl compounds (assuming monomers).



$$K = \frac{[\text{YC}_6\text{H}_4\text{Li}][\text{PhBr}]}{[\text{PhLi}][\text{YC}_6\text{H}_4\text{Br}]} \quad (\text{e})$$

where  $\text{Y} (K) = \text{p-Me}$  (0.6),  $\text{m-Me}$  (0.8),  $\text{p-Cl}$  (5.3),  $\text{m-CF}_3$  (289). The value of  $K$  for the  $\text{PhLi-MeC}_6\text{H}_4\text{Br-o}$  interaction is  $T$  independent.

5.5. Formation of Bonds between Elements of Groups IVB and IA 107  
 5.5.2. Carbon–Lithium Bonds  
 5.5.2.3. from Other Organolithiums

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**5.5.2.3.3. by Halogen–Lithium Exchange with Organic Halides.<sup>1,2</sup>**

The halogen–Li exchange:



is reversible, and equilibrium constants are known<sup>3,4</sup>, e.g., values for interaction of RLi and PhI:



where

$$K = \frac{[\text{PhLi}][\text{RI}]}{[\text{PhI}][\text{RLi}]} \quad (\text{c})$$

at  $-70^\circ\text{C}$  in  $\text{Et}_2\text{O}$  [ $\text{R}$  (log  $K$ ) =  $\text{CH}_2=\text{CH}$  (–2.41), cyclo- $\text{C}_3\text{H}_5$  (0.98), Et (3.5), n-Pr (3.9), t-BuCH<sub>2</sub> (6.1), cyclo- $\text{C}_5\text{H}_9$  (6.9)].

The values of  $K$  are similar in ether and in ether–pentane<sup>3</sup>. The different extents of aggregation also have little impact on  $K$ .

Values are also calculated for exchanges<sup>4</sup> involving aryl compounds (assuming monomers).



$$K = \frac{[\text{YC}_6\text{H}_4\text{Li}][\text{PhBr}]}{[\text{PhLi}][\text{YC}_6\text{H}_4\text{Br}]} \quad (\text{e})$$

where Y ( $K$ ) = p-Me (0.6), m-Me (0.8), p-Cl (5.3), m-CF<sub>3</sub> (289). The value of  $K$  for the PhLi–MeC<sub>6</sub>H<sub>4</sub>Br-o interaction is T independent.

At equilibrium, therefore, the Li becomes attached preferentially to the organic group best able to stabilize the negative charge. Hence, extensive exchanges and useful preparations are available from reaction of alkyl Li with aryl halides, cyclopropyl halides, alkenyl halides, alkynyl halides and  $\alpha$ -heterosubstituted alkyl halides (including per- and polyhaloalkanes), but not with simple alkyl halides; e.g., interaction of EtLi and MeI provides<sup>5</sup> a mixture of EtLi and MeLi.

The relative rates of halogen-Li exchange are  $I > Br > Cl > F$ . Few exchanges occur with chlorides, and fewer with fluorides. For Cl and F, the halogen-Li exchange is sufficiently slow to allow other reactions to occur, such as metallations of acidic ortho- or  $\alpha$ -hydrogens. Polychloroorganics, however, undergo Li-Cl exchange.

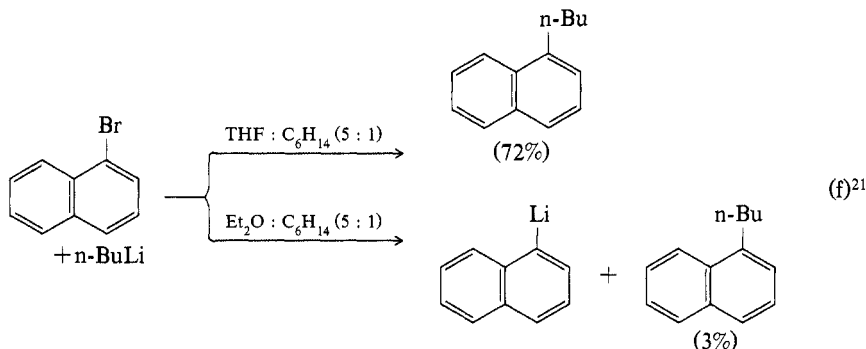
The relative reactivity of halides in halogen-Li exchanges with *n*-BuLi in tetrahydrofuran (THF) -C<sub>6</sub>H<sub>14</sub> at -100°C is<sup>6</sup>, ArCH<sub>2</sub>Br > ArBr > ArCH<sub>2</sub>CH<sub>2</sub>Br (RBr) > Ar(CH<sub>2</sub>)<sub>n</sub>Cl (Ar = aryl, R = alkyl).

Although the medium has little impact on the position of equilibrium, it does affect the rate. Halogen-Li exchanges are faster in ethers than in hydrocarbons<sup>3,7-8</sup>; LiX retards the Li-X exchange<sup>8</sup>.

Exchanges between aryl halides and aryllithiums are second order with four-center transition states<sup>2,7,9</sup>. A free-radical component, i.e., some homolytic fission, is detected in some reactions<sup>10-12</sup>, e.g., of alkyl halides and alkyllithium. However, the complete retention of configuration, e.g., of cycloalkyl<sup>13</sup> and alkenyl<sup>14</sup> halides, and the partial retention in others, e.g., of chiral alkyl halides<sup>15</sup>, suggest that the radical component is small.

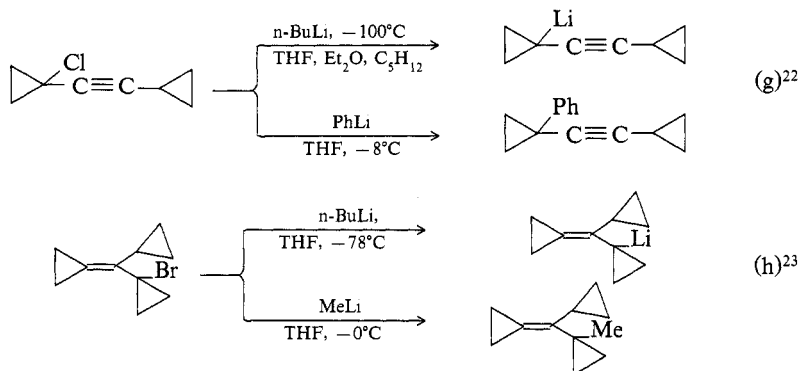
A side reaction may be metallation of hydrogens in positions ortho or  $\alpha$  to the halogen. The fast rates of halogen-Li exchanges, especially in cold electron-donating solvents, enable low T to be used and the extent of the slower metallations to be minimized. The presence of tetramethylethylenediamine (TMED) however, can promote metallations more than metal-hydrogen exchanges<sup>16</sup>.

Another problem can be alkylation, i.e., formation of coupled products RR' from RLi and R'Br, which occurs<sup>17-21</sup> more readily in THF than in Et<sub>2</sub>O (or nonpolar solvents); e.g.:



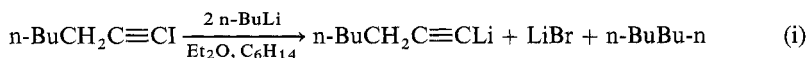
The exchange products 1-Li-naphthalene and *n*-BuBr form initially and then react to give the coupled product<sup>21</sup>. The coupling proceeds more readily with primary alkyl Li than with *s*- or *t*-alkyl-Li. Some alkylation occurs even at -70°C in THF with 2,7-Br<sub>2</sub>-naphthalene and *n*-BuLi; the major reaction is formation of 2,7-Li<sub>2</sub>-naphthalene.

More alkylation occurs using MeLi or PhLi than n-BuLi, e.g., in:

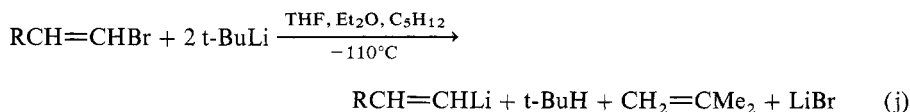


Alkylation occurs more readily with (E)-n-BuCH=CHBrSiMe<sub>3</sub> than with the (Z) isomer<sup>24</sup> using n-BuLi in THF; no alkylation occurs with s-BuLi in THF.

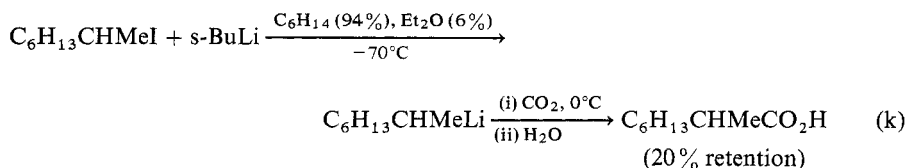
Use of 2 equiv of RLi—the additional mole of RLi is present to react preferentially with the RX formed in the halogen–Li step—overcomes the alkylation; e.g., with alkynyl iodides<sup>25</sup>:



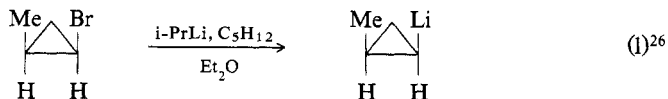
and with alkenyl bromides and t-BuLi<sup>14</sup>:

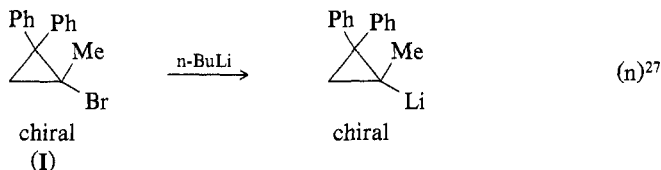
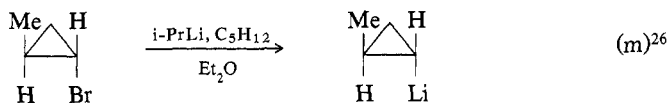


(i) Alkylolithiums. Reactions of simple alkyl halides and alkylolithiums are not used synthetically because of unfavorable equilibria and coupling and elimination side reactions. However, these reactions are used to study mechanistic aspects; e.g., the reaction of chiral 2-octyl iodide and s-BuLi in C<sub>6</sub>H<sub>14</sub>–Et<sub>2</sub>O at –70°C proceeds with partial retention of configuration<sup>15</sup>:

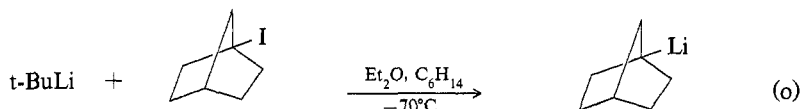


Cyclopropyl halides, however, and alkylolithiums react to give good yields of cyclopropyl-lithiums. Retention of configuration is found in cyclopropyl halide–alkyl–Li reactions; e.g.:



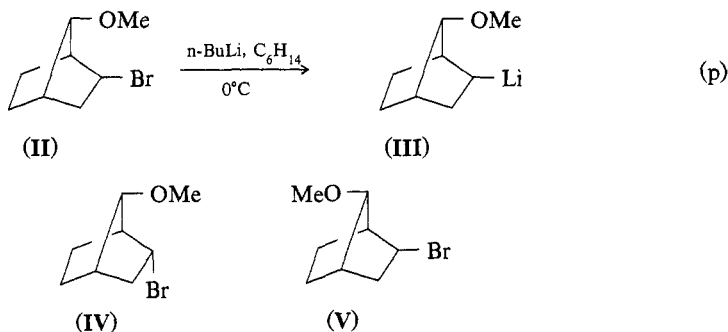


In contrast to Eq. (n), the reaction between **I** and Li leads to racemic products. Bridgehead tertiary alkylolithiums, such as 1-Li-triptycene<sup>28</sup>, 1-Li-norbornane<sup>29</sup>, 1-Li-bicyclo[2.2.2]octane<sup>28,29</sup> and 1-Li-adamantane<sup>29</sup>, may be formed via halogen–Li exchange, e.g.:



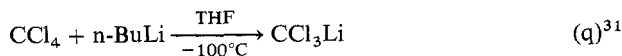
1-Lithionorbornane also forms from 1-iodonorbornane and either *s*-BuLi or 1-lithiobicyclo[2.2.2]octane<sup>29</sup>.

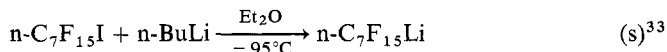
The halogen–Li exchange of **II** with *n*-BuLi to give **III** is faster<sup>30</sup> than the corresponding reactions of either **IV** or **V** owing to the stabilization of the product by intramolecular coordination of the OMe group and Li:



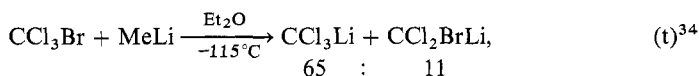
Lithium–halogen exchange of **IV** is the slowest.

Low T is used for halogen–Li exchanges involving polyhaloalkanes and alkylolithiums to avoid decomposition of the haloalkylolithiums. The reactivity is  $1 > \text{Br} > \text{Cl} > \text{F}$ , and even chlorides in polychloro-substituted alkanes can be substituted:



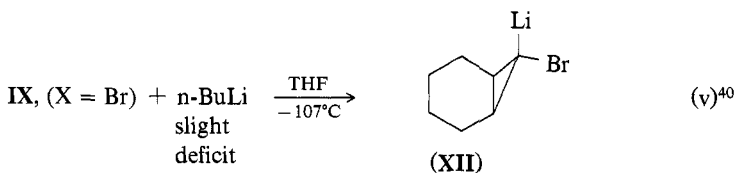
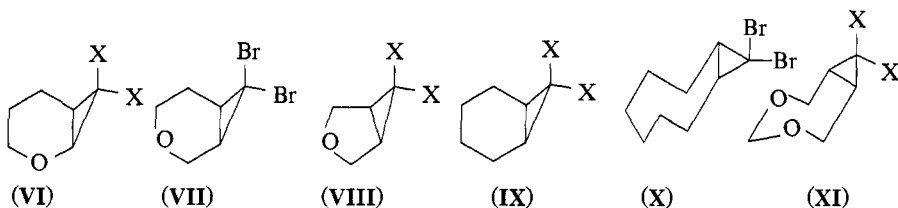


Where both Cl and Br are present in the polyhaloalkanes, products containing both halogens can be obtained as a consequence of scrambling and exchange, e.g.:



Halogen exchange also can occur<sup>35,36</sup> between LiX and the perhaloalkyllithium, e.g., with LiBr and  $[(\text{EtO})_2\text{PO}]\text{CCl}_2\text{Li}$ .

gem-Dihalocyclopropanes react with RLi stereoselectively if not stereospecifically, although subsequent isomerization may result<sup>37</sup>. Compounds VI, (X = Br)<sup>38,39</sup> VII<sup>38</sup>, VIII, (X = Cl)<sup>38</sup> IX, (X = Br)<sup>40,41</sup> X<sup>42</sup> and XI<sup>43</sup> undergo halogen-Li exchange stereospecifically at the endo position:



However at low T or with xs n-BuLi, X partially isomerizes to the exo isomer<sup>40</sup>. Both isomers are obtained from IX (X = Cl) and n-BuLi in THF-Et<sub>2</sub>O-C<sub>6</sub>H<sub>14</sub> at -115°C, the exo isomer being the major one (by a factor of 3-4)<sup>44</sup>. Endo-lithiation of VI, (X = Cl) occurs in Et<sub>2</sub>O, whereas the endo:exo lithiation ratio in THF is ca. 1.6:1. Halogen-Li exchange of VIII (X = Br) provides 9:1 endo:exo isomers. These isomers are configurationally stable<sup>45</sup>.

Among the compounds produced by the halogen-metal exchange route are  $\alpha$ -substituted alkylolithiums, where the  $\alpha$ -substituent is RS<sup>46</sup>, RSe<sup>47</sup>, RO<sub>2</sub>C<sup>48</sup>, R<sub>3</sub>Si<sup>49-50</sup>, R<sub>3</sub>Ge<sup>49</sup>, R<sub>3</sub>Sn<sup>51</sup> or R<sub>3</sub>Pb<sup>52</sup> (see Table 1).



TABLE 1. FORMATION OF SUBSTITUTED ALKYL LITHIUMS VIA HALOGEN-LITHIUM EXCHANGE

Compound	Lithiating conditions	Product	Refs.
$\text{CCl}_4$	n-BuLi, THF, $-100^\circ\text{C}$	$\text{CCl}_3\text{Li}$	53
$\text{CH}_2\text{Br}_2$	s-BuLi, THF, $\text{C}_6\text{H}_{14}$ , $\text{Et}_2\text{O}$ , $-110^\circ\text{C}$	$\text{BrCH}_2\text{Li}$	54
$\text{CFBr}_3$	n-BuLi, THF, $\text{C}_2\text{H}_{14}$ , $-116^\circ\text{C}$	$\text{CFBr}_2\text{Li}$	55
$\text{CBr}_4$	n-BuLi, THF, $\text{C}_3\text{H}_{12}$ , $-100^\circ\text{C}$	$\text{CBr}_3\text{Li}$	56
$\text{Cl}_3\text{CP(O)(OEt)}_2$	n-BuLi, THF, $\text{Et}_2\text{O}$ , $-105^\circ\text{C}$	$\text{LiCCl}_2\text{P(O)(OEt)}_2$	57
$\text{Cl}_2\text{CP(O)(OEt)}_2$	n-BuLi, THF, $-80^\circ\text{C}$	$\text{LiCClP(O)(OEt)}_2$	58
$\text{n-BuCl}_2\text{CP(O)(OEt)}_2$	n-BuLi, THF, $\text{Et}_2\text{O}$ , $-100^\circ\text{C}$	$\text{n-BuCClP(O)(OEt)}_2$	59
$\text{PhCCl}_3$	n-BuLi, THF, $\text{C}_6\text{H}_{14}$ , $-100^\circ\text{C}$	$\text{PhCCl}_2\text{Li}$	53
$\text{n-BuCBr}_3$	n-BuLi, LiBr, THF, $\text{Et}_2\text{O}$ , $-100^\circ\text{C}$	$\text{n-BuCBr}_2\text{Li}$	60
$\text{n-BuCHBr}_2$	n-BuLi, THF, $\text{Et}_2\text{O}$ , $-113^\circ\text{C}$	$\text{n-BuCHBrLi}$	61
$\text{CH}_2\text{BrCl}$	n-BuLi, THF, $\text{Et}_2\text{O}$ , $\text{C}_3\text{H}_{12}$ , $-110^\circ\text{C}$	$\text{CH}_2\text{ClLi}$ (+ some $\text{CHBrClLi}$ )	62
$\text{Ph}_3\text{SiCH}_2\text{Br}$	n-BuLi, $\text{Et}_2\text{O}$ , $-78^\circ\text{C}$	$\text{Ph}_3\text{SiCH}_2\text{Li}$	63
$\text{Me}_3\text{SiCCl}_2\text{Bu-n}$	s-BuLi, THF, $\text{Et}_2\text{O}$ , $-100^\circ\text{C}$	$\text{Me}_3\text{SiCClLiBu-n}$	64
$(\text{Me}_3\text{Si})_2\text{CBr}_2$	n-BuLi, THF, $\text{C}_6\text{H}_{14}$ , $-115^\circ\text{C}$	$(\text{Me}_3\text{Si})_2\text{CBrLi}$	65
$(\text{Me}_3\text{Si})_2\text{CBr}$	n-BuLi, $\text{Et}_2\text{O}$ , $\text{C}_6\text{H}_{14}$ , $-75^\circ\text{C}$	$(\text{Me}_3\text{Si})_3\text{CLi}$	65
$\text{Cl}_3\text{SiCCl}_2\text{SiCl}_3$	n-BuLi, THF, $\text{Et}_2\text{O}$ , $-100^\circ\text{C}$	$\text{Cl}_3\text{SiCClLiSiCl}_3$	66
$\text{Ph}_3\text{GeCH}_2\text{Br}$	n-BuLi, $\text{Et}_2\text{O}$ , $20^\circ\text{C}$	$\text{Ph}_3\text{GeCHLi}$	63
$\text{Ph}_3\text{SnCHLi}_2$	n-BuLi, $\text{Et}_2\text{O}$ , $-60^\circ\text{C}$	$\text{Ph}_3\text{SnCHLi}$	67
$\text{Me}_3\text{SnCBr}_3$	n-BuLi, THF, $\text{Et}_2\text{O}$ , $\text{C}_6\text{H}_{14}$ , $-100^\circ\text{C}$	$\text{Me}_3\text{SnCBr}_2\text{Li}$	68

## 5.5.2. Carbon-Lithium Bonds

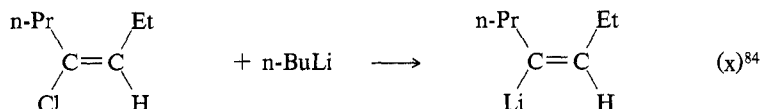
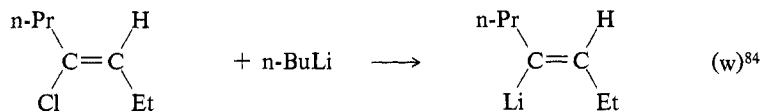
## 5.5.2.3. from Other Organolithiums

## 5.5.2.3.3. by Halogen-Lithium Exchange with Organic Halides.

Ph <sub>3</sub> PbCH <sub>2</sub> I	n-BuLi, Et <sub>2</sub> O, -50°C	Ph <sub>3</sub> PbCH <sub>2</sub> Li	69
C <sub>3</sub> F <sub>7</sub> I	MeLi, Et <sub>2</sub> O, -74°C	C <sub>3</sub> F <sub>7</sub> Li	70
1-Adamantane	t-BuLi, Et <sub>2</sub> O, -45°C	1-Lithioadamantane	71
BrCHCO <sub>2</sub> Et	n-BuLi	LiCH <sub>2</sub> CO <sub>2</sub> Et	72
PhSCH(C <sub>6</sub> H <sub>13</sub> )Br	n-BuLi, THF, -78°C	PhSCH(C <sub>6</sub> H <sub>13</sub> )Li	73
PhSeCH <sub>2</sub> Br	n-BuLi, THF, -78°C	PhSeCH <sub>2</sub> Li	74
CH(CH <sub>2</sub> ) <sub>4</sub> CHCBr <sub>2</sub> SMc	n-BuLi, THF, -90°C	CH(CH <sub>2</sub> ) <sub>4</sub> CHCLiSMc	75
CH(CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>2</sub> )CHCHCHBr	n-BuLi, Et <sub>2</sub> O, 0°C	CH(CH <sub>2</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHCHCHLi	76
cis-MeOCHCH <sub>2</sub> CHBr	t-BuLi, C <sub>3</sub> H <sub>12</sub> , -78°C	cis-MeOCHCH <sub>2</sub> CHLi	77
trans-MeOCHCH <sub>2</sub> CHBr	t-BuLi, C <sub>3</sub> H <sub>12</sub> , -78°C	trans-MeOCHCH <sub>2</sub> CHLi	77
PhCHCH <sub>2</sub> CFBr	n-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub>	PhCHCH <sub>2</sub> CFLi	78
EtOCHCH <sub>2</sub> CBBr <sub>2</sub>	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , -95°C	EtOCHCH <sub>2</sub> CLiBr <sup>a</sup>	79
Me <sub>2</sub> NCOCMeCH <sub>2</sub> CBBr <sub>2</sub>	MeLi, Et <sub>2</sub> O, -60°C	Me <sub>2</sub> NCOCMeCH <sub>2</sub> CBRLi <sup>b</sup>	80
CHCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CHCBrCl(exo-Cl)	MeLi, Et <sub>2</sub> O, THF, -78°C	CHCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CHCLiCl(exo-Cl)	81
CHCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CHCBrC(exo-Br)	MeLi, Et <sub>2</sub> O, THF, -78°C	CHCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CHCLiCl(exo-Li)	81
CHCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CHCCl <sub>2</sub>	n-BuLi, Et <sub>2</sub> O, -78°C	CHCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> CHCHLiCl (exo-Cl)	82
HCBBr <sub>2</sub> CH = NBut	n-BuLi, THF, -70°C	[HCBBr - CH - NBut]Li	83

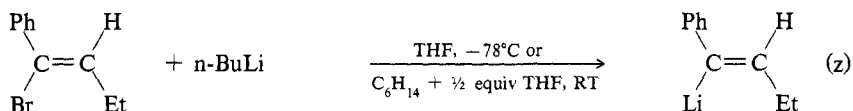
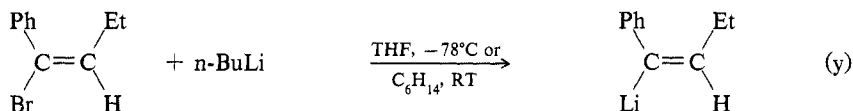
<sup>a</sup> Li cis to EtO group.<sup>b</sup> Li cis to Me<sub>2</sub>NCO group.

(ii) Alkenyllithiums. Halogen–Li exchanges of vinyl halides with RLi proceed with retention of configuration<sup>14,84,85</sup>, e.g.:



In contrast to the stereospecific reactions using n-BuLi, reaction with Li lead to both isomers, a consequence of the radical nature of the Li reaction<sup>84</sup>.

Retention of configuration results in the reactions of PhBrC=CEtH with n-BuLi under controlled conditions<sup>85</sup>:

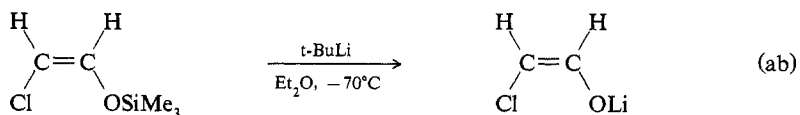
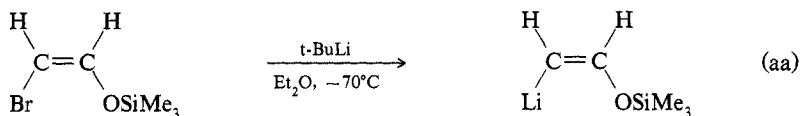


However, at  $> -78^\circ\text{C}$  in THF or on increasing the amount of THF present in the hexane at RT, isomerization results.

The halogen–Li exchanges between  $\text{Me}_3\text{SiCX}=\text{CHR}$  (**XIII**) ( $\text{R} = \text{n-Bu}$ , cyclo- $\text{C}_6\text{H}_{11}$  or  $\text{t-Bu}$ ;  $\text{X} = \text{Br}$  or  $\text{I}$ ) and n-BuLi proceeds stereoselectively rather than stereo- specifically<sup>86</sup>. Reactions of (Z)-**XIII** ( $\text{X} = \text{Br}$ ) proceed at  $-95^\circ\text{C}$  in  $\text{THF-Et}_2\text{O-C}_6\text{H}_{14}$ ; reactions of (Z)-**XIII** ( $\text{X} = \text{I}$ ) occur in  $\text{Et}_2\text{O}$  at  $-70^\circ\text{C}$ . The more hindered (E) isomers react slower.

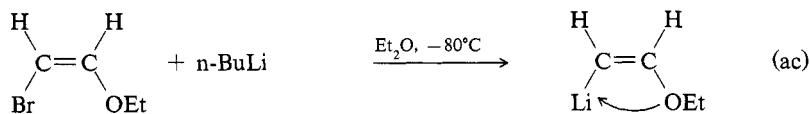
Vinyl chlorides react more sluggishly than bromides and iodides. Equations (w)–(x) show that chloride–lithium exchanges can work well, but with side reactions. The major alternative to Cl–Li exchange is metallation of the acidic  $\alpha$  hydrogen<sup>87</sup> (see §5.5.2.3.2), which occurs with vinyl fluorides if no other halogen is present.

Different rates of Cl–Li and Br–Li exchanges are shown by<sup>88</sup> (Z)- $\text{Me}_3\text{SiOCH}=\text{CHX}$ , where  $\text{X} = \text{Cl}$ , Br:

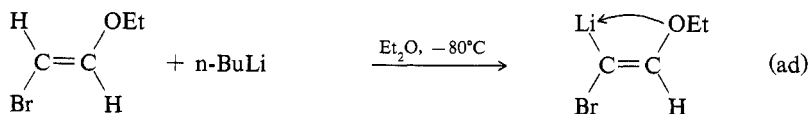


Normal Br–Li exchange occurs with the bromide, but Si–O cleavage results with the chloride.

The choice of reaction of vinylic bromides with *n*-BuLi can be governed by donor groups; e.g., Br–Li exchange occurs<sup>89</sup> with (Z)CHBr=CHOEt at  $-80^{\circ}\text{C}$  in  $\text{Et}_2\text{O}$ :



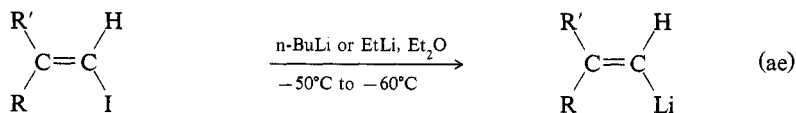
whereas metallation occurs with the (E) isomer:



The reactions lead to vinyllithiums, stabilized by intramolecular coordination. Use of  $[\text{PhPh}]^-\text{Li}^+$  with (E)-CHBr=CHOEt, however, provides (E)-LiCH=CHOEt.

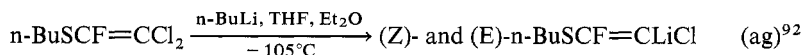
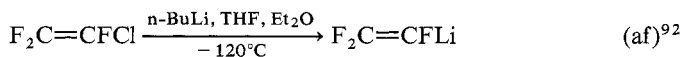
The use of 2 equiv of *t*-BuLi is recommended<sup>14</sup> for halogen–Li exchange of vinylic bromides, the additional mole being used to react with and so destroy the released organic bromide, *t*-BuBr [see Eq. (i)].

Vinylic iodides are used<sup>19</sup> in  $\text{Et}_2\text{O}$ :



where  $\text{R} = \text{Et}, \text{C}_7\text{H}_{15}$ , not Me;  $\text{R}' = \text{H}, \text{Et}, n\text{-Bu}$ . However, in THF coupling results to form  $\text{RR}'\text{C}=\text{CHR}$  ( $\text{R} = n\text{-Bu}$  or  $\text{Et}$ )<sup>20</sup>.

Halogen–Li exchanges occur for substituted vinylic halides, e.g., alkyl<sup>14,19,84</sup>, aryl<sup>85,90</sup>, alkoxy<sup>90,91</sup>, halo (including perhaloalkenes)<sup>92–95</sup>, carboxy<sup>96–98</sup>, amino<sup>99</sup>, carboxyamido<sup>100</sup> and  $\text{Me}_3\text{Si}$ <sup>86,101</sup> substituents (see Table 2). The perhaloalkenyl compounds require low *T* to intercept these thermally labile organolithiums. When more than one vinylic halogen is present, the preference for exchange is  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ , e.g.:



Other unsaturated organolithiums that can be formed by halogen–Li exchanges include allyllithiums, e.g.,  $[\text{CF}_2\cdots\text{CH}\cdots\text{CH}_2]\text{Li}^+$ <sup>128</sup> and allenyllithiums<sup>129</sup>:

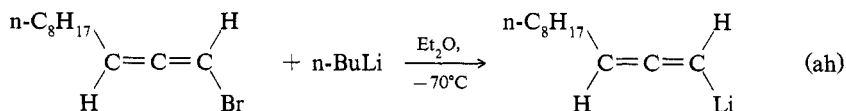

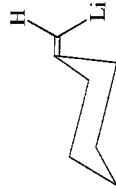
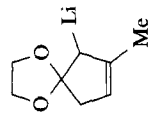
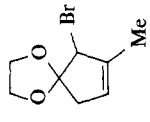


TABLE 2. FORMATION OF VINYL LITHIUMS VIA HALOGEN-LITHIUM EXCHANGE

Compound	Lithiating conditions	Product	Refs.
(Z)-CHBr=CHOEt	n-BuLi, Et <sub>2</sub> O, -80°C	(Z)-CHLi=CHOEt	89
CH <sub>2</sub> =CHBr	2 equiv t-BuLi, THF, Et <sub>2</sub> O, -110°C	CH <sub>2</sub> =CHLi	102
(E)-PhCH=CHBr	2 equiv t-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -110°C	(E)-PhCH=CHLi	102
(Z)-PhCH=CHBr	2 equiv t-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -110°C	(Z)-PhCH=CHLi	102
CH <sub>2</sub> =CPhBr	2 equiv t-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -110°C	CH <sub>2</sub> =CPhLi	102
CH <sub>2</sub> =CBrCH <sub>2</sub> OH	2.5 equiv t-BuLi, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -78°C to 0°C	CH <sub>2</sub> =CLiCH <sub>2</sub> OLi	103
O(CH <sub>2</sub> ) <sub>2</sub> OCCH <sub>2</sub> CH=CHBr	1.3 equiv n-BuLi, THF, -78°C	O(CH <sub>2</sub> ) <sub>2</sub> OCCH <sub>2</sub> CH=CHLi	104
C(OMe) <sub>2</sub> CH=CHC(OMe) <sub>2</sub> CH=CHBr	n-BuLi, THF, -70°C	C(OMe) <sub>2</sub> CH=CHC(OMe) <sub>2</sub> CH=CHLi	105
MeOCBr=CHOMe	n-BuLi, Et <sub>2</sub> O	MeOCLi=CHOMe	107
Me <sub>3</sub> C=CBrCH(OEt) <sub>2</sub>	n-BuLi, -90°C	Me <sub>3</sub> C=CLiCH(OEt) <sub>2</sub>	108
(Z)-Me <sub>3</sub> SiOCH=CHBr	t-BuLi, Et <sub>2</sub> O, -70°C	(Z)-Me <sub>3</sub> SiOCH=CHLi	109
	t-BuLi, THF, -90°C		106
(S)-(+)			
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> OCH=CHBr	t-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -110°C	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> OCH=CHLi	110
Ph <sub>2</sub> C=CBrCO <sub>2</sub> H	2 equiv n-BuLi, THF, -100°C	Ph <sub>2</sub> C=CLiCO <sub>2</sub> Li	111
Me <sub>2</sub> C=CBrCO <sub>2</sub> H	2 equiv n-BuLi, THF, -100°C	Me <sub>2</sub> C=CLiCO <sub>2</sub> Li	112

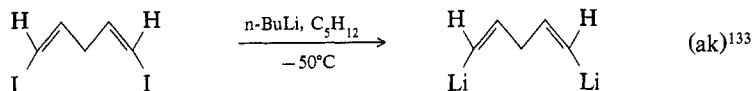
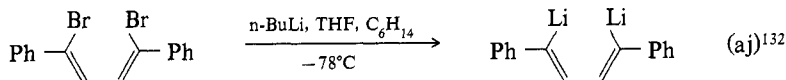
(E)-PhCH=CBrCO <sub>2</sub> H	n-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -115°C	(E)-PhCH=CLiCO <sub>2</sub> Li	113
(Z)-BrCH=CMcCO <sub>2</sub> H	2 equiv n-BuLi, THF, Et <sub>2</sub> O, C <sub>5</sub> H <sub>12</sub> , -115°C	(Z)-LiCH=CMcCO <sub>2</sub> Li	114
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> C(CONMe <sub>2</sub> )=CBr	t-BuLi, THF, C <sub>6</sub> H <sub>12</sub> , -75°C	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> C(CONMe <sub>2</sub> )=CLi	115
(E)-Me <sub>2</sub> NCPH=CHBr	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , -70°C	(E)-Me <sub>2</sub> NCPH=CHLi	116
O-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> CBr=CNMe <sub>2</sub>	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , -70°C	O-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> CLi=CNMe <sub>2</sub>	116
CH <sub>2</sub> =CBrSiMe <sub>3</sub>	t-BuLi, THF, -78°C	CH <sub>2</sub> =C(SiMe <sub>3</sub> )Li	117
(Z)-n-BuCH=CBr-SiMe <sub>3</sub>	n-BuLi, THF, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , -95°C	(Z)-n-BuCH=CLi(SiMe <sub>3</sub> )	118
CH <sub>2</sub> =CBrCF <sub>3</sub>	n-BuLi, Et <sub>2</sub> O, -78 to 90°C	CH <sub>2</sub> =CLiCF <sub>3</sub>	119
(Z)-PhC(CF <sub>3</sub> )=CFBr	n-BuLi, THF, C <sub>6</sub> H <sub>14</sub> , -78°C	(E)-PhC(CF <sub>3</sub> )=CFLi	120
Ph <sub>2</sub> C=CBr <sub>2</sub>	n-BuLi, THF, C <sub>5</sub> H <sub>12</sub> , -100°C	Ph <sub>2</sub> C=CBrLi	121
F <sub>2</sub> C=CFBr	2 equiv t-BuLi, Et <sub>2</sub> O, -110°C	CF <sub>2</sub> =CFLi	102
Cl <sub>2</sub> C=CF(SBu-n)	n-BuLi, Et <sub>2</sub> O, THF, -105°C	(E)- and (Z)-LiCCl=CF(SBu-n)	122
Cl <sub>2</sub> C=CClBr	n-BuLi, Et <sub>2</sub> O, -110°C	Cl <sub>2</sub> C=CCLi	123
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CBr=CBBr	n-BuLi, Et <sub>2</sub> O, -70°C	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CBr=CLi	124
CClCCl=CClCCl(CCl <sub>2</sub> )CBr=CBBr	n-BuLi, Et <sub>2</sub> O, -75°C	CClCCl=CClCCl(CCl <sub>2</sub> )CBr=CLi	125
Me <sub>2</sub> C=C=CHBr	n-BuLi, Et <sub>2</sub> O, -70°C	Me <sub>2</sub> C=C=CHLi	126
	n-BuLi, THF, -78°C		127
			

and alkynyllithiums<sup>130,131</sup>,



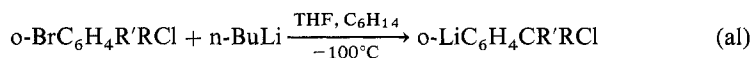
where X = Cl or Br. Such routes to alkynyllithiums are not useful because other precursors, in particular the terminal alkynes themselves, are more readily available.

$\alpha,\omega$ -Dihalobuta-1,3-dienes and -penta-1,4-dienes react with *n*-BuLi at low T to provide the corresponding dilithio derivatives, e.g.:

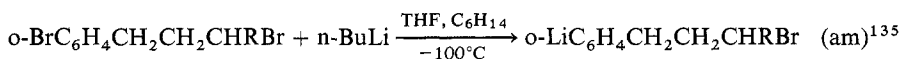


Bromocyclooctatetraene also reacts by Br-Li exchange with *n*-BuLi to give lithio-cyclooctatetraene<sup>134</sup>.

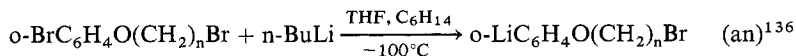
(iii) Phenyllithiums. The sequence of halogen-Li exchanges<sup>6</sup> is  $\text{ArCH}_2\text{Br} > \text{ArBr} > \text{ArCH}_2\text{CH}_2\text{Br}$  ( $\text{RBr}$ )  $> \text{Ar}(\text{CH}_2)_n\text{Cl}$  ( $\text{RCl}$ ) ( $\text{Ar}$  = aryl,  $\text{R}$  = alkyl). Thus the aryl halogen is exchanged preferentially in:



where  $\text{R} = \text{R}' = \text{H}$ <sup>6</sup> or  $\text{R} = \text{H}$  or  $\text{Me}$  and  $\text{R}' = \text{Me}$ <sup>135</sup>;



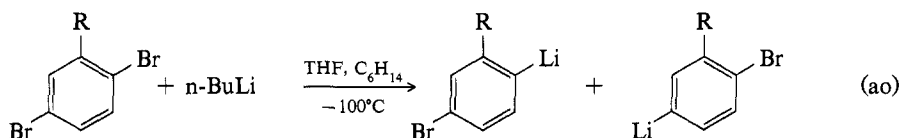
where  $\text{R} = \text{H}$  or  $\text{Me}$ ;



where  $n = 2$  or  $3$ ; but not in<sup>6</sup>  $o\text{-BrC}_6\text{H}_4\text{CH}_2\text{Br}$ .

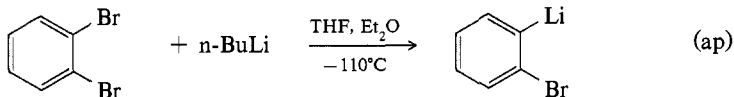
A Br is exchanged in preference to Cl or F in benzenoid compounds<sup>137</sup>, e.g., in 2-F-4-Cl-C<sub>6</sub>H<sub>3</sub>Br.

The Br-Li exchange in 2,5-Br<sub>2</sub>C<sub>6</sub>H<sub>3</sub>R is selective<sup>138</sup>:



R	Relative %
NHLi	0:100
Me	30:70
CO <sub>2</sub> Li	90:10
NMe <sub>2</sub>	95:5
NO <sub>2</sub>	100:0

Both halogens in di-bromo- or di-iodobenzene derivatives can be replaced by Li in halogen-Li exchanges<sup>2</sup>. If the two halogens are ortho, aryne formation can occur from the monoexchange product, 1-Li-2-X-benzene, although such compounds can be trapped at low T, e.g.<sup>139</sup>:

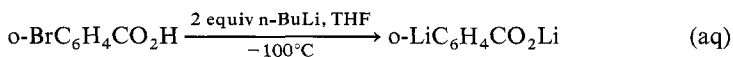


Functional groups are tolerated in the halogen-Li exchanges, although side reactions may limit yields. Low T and electron-donating solvents limit competition to X-Li exchanges from ortho-metallations or reactions with the functional group. Ortho-metallation to Cl or F in halobenzenes is favored over halogen-Li exchange (except with polychloro compounds). Bromoarenes containing powerful ortho-directing groups may undergo metallations ortho to Y, as well as Br-Li exchange, e.g.,  $\text{BrC}_6\text{H}_4\text{OMe}$  and  $n\text{-BuLi}$ <sup>2,140</sup>. More halogen-Li exchanges occur with  $n\text{-BuLi}$  than with either  $\text{MeLi}$  or  $\text{PhLi}$ , which favor metallations<sup>2</sup>.

The functional groups tolerated include  $\text{OH}$ <sup>1</sup>,  $\text{SH}$ <sup>1,141</sup>,  $\text{NO}_2$ <sup>138,142,143</sup>,  $\text{NH}_2$ <sup>1</sup>,  $\text{NHCOR}$  ( $\text{R} = t\text{-Bu}$  or  $\text{CF}_3$ )<sup>144</sup>,  $\text{SO}_2\text{NH}_2$ <sup>1</sup>,  $\text{SO}_2\text{NR}_2$ <sup>1</sup>,  $\text{CN}$ <sup>145,146</sup>,  $\text{CO}_2\text{H}$ <sup>141,147</sup>,  $\text{CO}_2\text{Me}$ <sup>148</sup>,  $\text{CO}_2\text{Bu-}t$ <sup>149</sup>,  $(\text{CH}_2)_n\text{CO}_2\text{H}$ <sup>150</sup>,  $\text{CH}_2\text{CN}$ <sup>145</sup> and epoxides<sup>151,152</sup>.

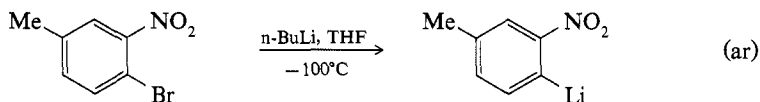
Acidic hydrogens, e.g.,  $\text{OH}$ ,  $\text{SH}$ ,  $\text{NH}_2$  and  $\text{CO}_2\text{H}$ , are metallated during the course of the reaction with  $\text{RLi}$  (and hence 2 equiv of  $\text{RLi}$  are necessary), but these groups can be recovered on workup.

The compounds o-, m-, and p- $\text{BrC}_6\text{H}_4\text{CO}_2\text{H}$  undergo Br-Li exchanges with  $n\text{-BuLi}$  in THF at  $-100^\circ\text{C}$ , e.g.:



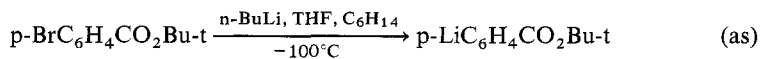
At  $-20^\circ\text{C}$ , self-condensation and destruction of the aryllithium result.

Whereas o- $\text{NO}_2\text{C}_6\text{H}_4\text{Br}$  and other o-nitrobromoarenes undergo halogen-Li exchanges, e.g.<sup>142</sup>:



reactions with the m- or p-isomers are not useful because redox reactions occur with  $n\text{-BuLi}$ .

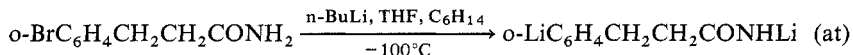
Halogen-metal exchange also occurs with o- $\text{MeO}_2\text{CC}_6\text{H}_4\text{Br}$  at  $-100^\circ\text{C}$ , but for the m- or p-analogues<sup>148</sup> condensations arise even at this T, and it is not possible to trap the initial aryllithium. The more hindered p- $\text{LiC}_6\text{H}_4\text{CO}_2\text{Bu-}t$  can be intercepted from the reaction of p- $\text{BrC}_6\text{H}_4\text{CO}_2\text{Bu-}t$  and  $n\text{-BuLi}$  at  $-100^\circ\text{C}$ :



The aryllithium product, p- $\text{LiO}_2\text{CCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Li}$ , can be trapped<sup>150</sup> from the reaction of p- $\text{HO}_2\text{CCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Br}$  with  $n\text{-BuLi}$ ; the product from the reaction of o- $\text{HO}_2\text{CCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Br}$ , viz., o- $\text{LiO}_2\text{CCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Li}$ , cyclizes even at  $-100^\circ\text{C}$ .

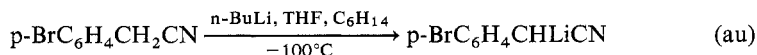


Cyclization of  $o\text{-LiC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CONPr-i}_2$  also occurs, but  $o\text{-LiC}_6\text{H}_4\text{CH}_2\text{-CH}_2\text{CONHLi}$  is stable<sup>150</sup> at  $-100^\circ\text{C}$ :

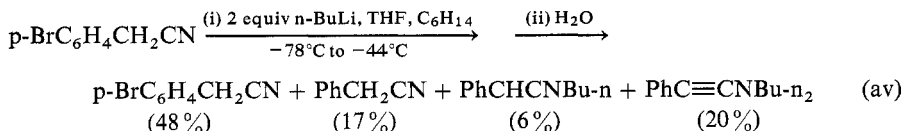


More complex reaction mixtures can arise<sup>150</sup> with  $o$ - or  $p$ - $\text{BrC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}$ . Reactions with  $n\text{-BuLi}$  lead to both  $\text{Br-Li}$  and  $\text{H-Li}$  exchanges; among the products is the trianionic  $\text{LiC}_6\text{H}_4\text{CHLiCO}_2\text{Li}$ . The trianions slowly react with the solvent (THF) to provide  $\text{LiC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{Li}$ , i.e., the products expected from the direct  $\text{Br-Li}$  exchanges of  $\text{BrC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}$ .

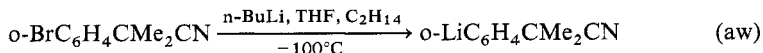
The cyanomethyl compounds,  $o$ -,  $m$ -, or  $p$ - $\text{BrC}_6\text{H}_4\text{CH}_2\text{CN}$ , are metallated at  $-100^\circ\text{C}$  in THF at the benzylic position in preference to  $\text{Br-Li}$  exchange, e.g.<sup>145</sup>:



Even with  $xs$   $n\text{-BuLi}$  at  $-78^\circ$ , little  $\text{Br-Li}$  exchange occurs, although at  $-44^\circ\text{C}$  some exchange does result, as well as alkylation, from the  $n\text{-BuBr}$  formed in the exchange:

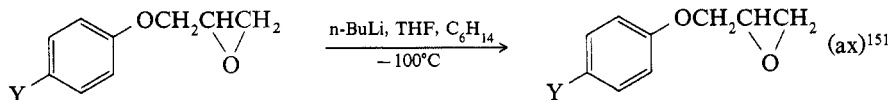


$\alpha$ -Cyanoalkylphenyl bromides containing no benzylic hydrogens undergo useful  $\text{B-Li}$  exchange, e.g.:

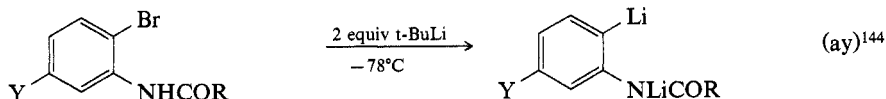


although alkylation becomes more serious as  $T$  is raised.

The three isomeric  $\text{LiC}_6\text{H}_4\text{CN}$  can be trapped<sup>145</sup> from  $\text{BrC}_6\text{H}_4\text{CN}$  with  $n\text{-BuLi}$  in THF,  $\text{C}_6\text{H}_{14}$  at  $-100^\circ\text{C}$ . Low  $T$  allows halogen-Li exchanges to occur with bromoaryl-substituted epoxides, e.g.:



where  $\text{Y} = \text{H Me, Ph, OMe or Cl}$  and amides:



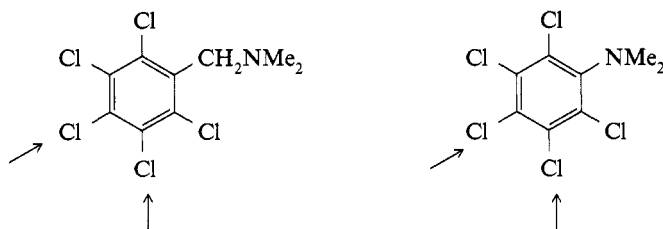
where  $\text{Y} = \text{H or MeO}$ ;  $\text{R} = t\text{-Bu or CF}_3$ .

Reactions between  $\text{ArBr}$  and  $\text{RLi}$  in hydrocarbons, although slower than in ethers, do have an advantage in that the aryllithiums precipitate and can be obtained in high yields and purity<sup>153,154</sup>.

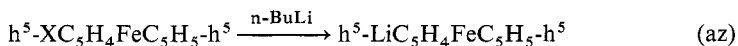
Table 3 lists aryllithiums formed by halogen–Li exchange.

(iv) Poly- and Perhalophenyllithiums. Poly- and perhalogenoarenes undergo halogen–Li exchanges (Cl but not F), although some ring metallation may occur for polychlorobenzenes. Metallations are more likely using  $\text{MeLi}$  or  $\text{PhLi}$  than using  $n\text{-BuLi}$  or  $t\text{-BuLi}$ . Hexafluorobenzene undergoes exclusive alkylation<sup>186,187</sup> with  $\text{RLi}$ .

The orientations of Cl–Li exchanges in  $\text{C}_6\text{Cl}_5\text{Y}$  and of H–Li exchanges in  $\text{C}_6\text{H}_5\text{Y}$  show differences; e.g., metallations of  $\text{C}_6\text{H}_5\text{CH}_2\text{NMe}_2$  and  $\text{C}_6\text{H}_5\text{NMe}_2$  occur ortho to the substituent groups, whereas Cl–Li exchanges of the perchloro analogues using  $n\text{-BuLi}$  in  $\text{Et}_2\text{O}$  at  $-170^\circ\text{C}$  are<sup>188,189</sup>:



(v) Ferrocenyllithiums. Monohalo-<sup>190</sup> and perchloroferrocenes<sup>191</sup> undergo halogen–Li exchanges in good yields, e.g.:



where  $\text{X} = \text{Br}$  or  $\text{I}$ .

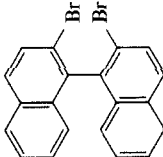
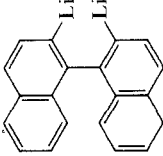
(vi) Heteroaryllithiums. Halogen–Li exchange yields both five- and six-membered heterocyclic aryllithiums (see Table 4).

Halogen–metal exchange occurs with halothiophenes even at  $-70^\circ\text{C}$ , but lithiations of  $\beta$ -halothiophenes, including 3-Br and 3-I derivatives, can result (see §5.5.2.3.2). Exchanges of  $\alpha$ -Br or  $\alpha$ -I occur more readily than the corresponding  $\beta$ -halogen; I is more readily exchanged than Br.

For chlorothiophenes, Cl–Li exchange results only when no  $\alpha$  position is free, as with 2,5- $\text{Cl}_2$ -thiophene, but not with 2-Cl-thiophene, which provides 2-Cl,5-Li-thiophene with  $n\text{-BuLi}$ . Halogen–Li exchanges of 2-Cl,3-X-thiophene ( $\text{X} = \text{Br}$  or  $\text{I}$ ), 2-Br,4-I-thiophene and 2-Cl,4-Br-thiophene with  $n\text{-BuLi}$  at  $-70^\circ\text{C}$  all take place with the  $\alpha$ -halogens<sup>194</sup>. Tetrachlorothiophene reacts with  $n\text{-BuLi}$  in  $\text{Et}_2\text{O}$  at  $5\text{--}10^\circ\text{C}$  to give 2,5- $\text{Li}_2$ ,3,4- $\text{Cl}_2$ -thiophene<sup>206</sup>; controlled conditions lead to mono-exchange<sup>200</sup>.

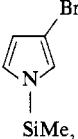
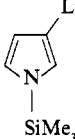
Halogen–Li exchange routes to lithiopyridines are especially valuable because metallations of pyridine derivatives are not available owing to the ease of addition of  $\text{RLi}$  to the  $\text{C}=\text{N}$  bond. Formation of 2- or 3-Li-pyridines from the corresponding bromides is possible using  $n\text{-BuLi}$  in THF or  $\text{C}_6\text{H}_{14}$  at  $-100^\circ\text{C}$ , and 2-Li-pyridine undergoes Br–Li

TABLE 3. FORMATION OF ARYL LITHIUMS VIA HALOGEN–LITHIUM EXCHANGE

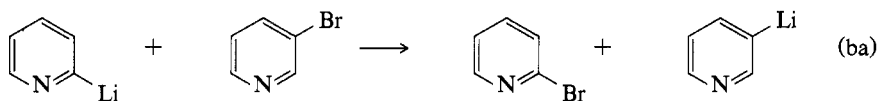
Compound	Lithiating conditions	Product	Refs.
<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	PhLi, THF, –100°C	<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Li	142
PhBr	<i>n</i> -BuLi, PhMe, 50°C	PhLi	153
2-1-6-MeC <sub>6</sub> H <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Me-6'-1-2'	<i>n</i> -BuLi, Et <sub>2</sub> O, –10°C	2-Li-6-MeC <sub>6</sub> H <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Me-6'-1-2'	155
3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Br	<i>n</i> -BuLi, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , 25°C	3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> Li	156
2,4,6-( <i>t</i> -Bu) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> Br	<i>n</i> -BuLi, THF, C <sub>6</sub> H <sub>14</sub> , –78°C	2,4,6-( <i>t</i> -Bu) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> Li	157
<i>m</i> -FC <sub>6</sub> H <sub>4</sub> Br	<i>n</i> -BuLi, Et <sub>2</sub> O, –45°C	<i>m</i> -FC <sub>6</sub> H <sub>4</sub> Li	158
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> Cl	<i>n</i> -BuLi, Et <sub>2</sub> O	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> Li	159
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> Br	<i>n</i> -BuLi, Et <sub>2</sub> O	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> Li	159
<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> Br	xs <i>n</i> -BuLi	<i>o</i> -LiC <sub>6</sub> H <sub>4</sub> Li	159
	<i>n</i> -BuLi, Et <sub>2</sub> O, THF, –100°C	<i>o</i> -LiC <sub>6</sub> H <sub>4</sub> Br	160
	<i>t</i> -BuLi, C <sub>6</sub> H <sub>14</sub>		161
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<i>n</i> -BuLi, Et <sub>2</sub> O, –60°C	<i>p</i> -LiNC <sub>6</sub> H <sub>4</sub> Li	162
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	<i>n</i> -BuLi, Et <sub>2</sub> O, 0°C	<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Li	163
<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> OH	2 equiv <i>n</i> -BuLi, Et <sub>2</sub> O, RT	<i>o</i> -LiOC <sub>6</sub> H <sub>4</sub> Li	164
<i>o</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> SH	<i>n</i> -BuLi, THF, C <sub>6</sub> H <sub>14</sub> , –100°C	<i>o</i> -LiSCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Li	165
<i>o</i> -XC <sub>6</sub> H <sub>4</sub> CHCH <sub>2</sub> O, X = Br or I	<i>n</i> -BuLi, THF, –78°C	<i>o</i> -LiC <sub>6</sub> H <sub>4</sub> CHCH <sub>2</sub> O	166

$\overline{\text{p-(OCH}_2\text{CHCH}_2\text{O)C}_6\text{H}_4\text{Br}}$	n-BuLi, $-100^\circ\text{C}$	$\overline{\text{p-(OCH}_2\text{CHCH}_2\text{O)C}_6\text{H}_4\text{Li}}$	167
o-HO $\text{C}_6\text{H}_4\text{Br}$	2 equiv n-BuLi, THF, $-78^\circ\text{C}$	o-LiO $\text{C}_6\text{H}_4\text{Li}$	168
p-Br $\text{C}_6\text{H}_4\text{(CH}_2\text{)}_2\text{CO}_2\text{H}$	2 equiv n-BuLi, THF, $-90^\circ\text{C}$ , THF, $\text{C}_6\text{H}_{14}$		
o-Br $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$	n-BuLi, Et $_2\text{O}$ , $-100^\circ\text{C}$ to $-78^\circ\text{C}$	p-Li $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{Li}$	169
2-MeO $\text{C}_2\text{-3-MeOC}_6\text{H}_3\text{Br}$	2 equiv n-BuLi, THF, $-95^\circ\text{C}$	o-Li $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$	170
m-NCC $\text{C}_6\text{H}_4\text{Br}$	n-BuLi, THF, $-100^\circ\text{C}$	2-MeO $\text{C}_2\text{-3-MeOC}_6\text{H}_3\text{Li}$	171
2-Br $\text{CH}_2\text{CH}_2\text{-4,5-(MeO)}_2\text{C}_6\text{H}_2\text{I}$	n-BuLi, $\text{C}_6\text{H}_{14}$ , $-100^\circ\text{C}$	m-NCC $\text{C}_6\text{H}_4\text{Li}$	172
o-XC $\text{C}_6\text{H}_4\text{CH=NC}_6\text{H}_{11}$ , X = Br or I	n-BuLi, THF, $\text{C}_6\text{H}_{14}$ , $-78^\circ\text{C}$	2-Br $\text{CH}_2\text{CH}_2\text{-4,5-(MeO)}_2\text{C}_6\text{H}_2\text{Li}$	173
o-Me $_2\text{AsCH}_2\text{C}_6\text{H}_4\text{Br}$	n-BuLi, PhH	o-Li $\text{-C}_6\text{H}_4\text{CH=NC}_6\text{H}_{11}$	174
1-Br-Naphthalene	n-PrLi, Et $_2\text{O}$		
2,7-Br $_2$ -Naphthalene	n-BuLi, Et $_2\text{O}$ , $20^\circ\text{C}$	o-Me $_2\text{AsCH}_2\text{C}_6\text{H}_4\text{Li}$	175
	n-BuLi, THF, $-35^\circ\text{C}$	1-Li-Naphthalene	176
5,6-Br $_2$ -Acenaphthene	n-BuLi, TMED, Et $_2\text{O}$ , $-10^\circ\text{C}$	2-Li-7-Br-Naphthalene	177
2-Bromophenanthrene	n-BuLi, Et $_2\text{O}$ , reflux	2,7-Li $_2$ -Naphthalene	178
1-Bromopyrene	PhLi, Et $_2\text{O}$ , PhH, RT	5,6-Li $_2$ -Acenaphthene	179
2,3,4,5-Cl $_4\text{C}_6\text{HI}$	n-BuLi, Et $_2\text{O}$ , $-70^\circ\text{C}$	2-Li-Phenanthrene	180
C $_6\text{F}_5\text{Cl}$	n-BuLi, Et $_2\text{O}$ , $-70^\circ\text{C}$	2,3,4,5-Cl $_4\text{C}_6\text{HLi}$	181
C $_6\text{Cl}_6$	n-BuLi, Et $_2\text{O}$ , $-78^\circ\text{C}$ to $-10^\circ\text{C}$	C $_6\text{F}_5\text{Li}$	182
	3 equiv t-BuLi, THF, $-78^\circ\text{C}$	C $_6\text{Cl}_5\text{Li}$	183
	n-BuLi, Et $_2\text{O}$ , $-35^\circ\text{C}$	1,4-Li $_2\text{C}_6\text{Cl}_4$	184
		C $_6\text{Br}_3\text{Li}$	185

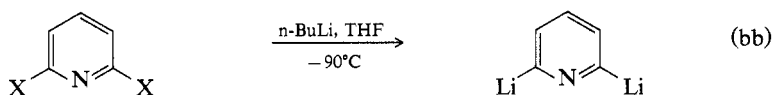
TABLE 4. FORMATION OF HETEROARYLLITHIUMS VIA HALOGEN–LITHIUM EXCHANGE

Compound	Lithiating conditions	Product	Refs.
3-Br-Thiophen	n-BuLi, Et <sub>2</sub> O, –70°C	3-Li-Thiophen	192
2,3-Br <sub>2</sub> -Thiophen	n-BuLi, Et <sub>2</sub> O, –70°C	2-Li-3-Br-Thiophene	192
4-Br-2-F-Thiophen	EtLi, Et <sub>2</sub> O, –70°C	4-Li-2-F-Thiophene	193
2-Cl-3-I-Thiophen	n-BuLi, Et <sub>2</sub> O, –70°C	2-Cl-3-Li-Thiophene	194
3-Br-Selenophen	PhLi, Et <sub>2</sub> O, reflux	3-Li-Selenophene	195
4-Br-1-Me-Pyrazole	PhLi, Et <sub>2</sub> O, –70°C	4-Li-1-Me-Pyrazole	196
3-Br-Furan	n-BuLi, C <sub>7</sub> H <sub>16</sub> , Et <sub>2</sub> O, –70°C	3-Li-Furan	197
3-Br-Benzo[b]furan	n-BuLi, Et <sub>2</sub> O, –70°C	3-Li-Benzo[b]furan	198
3-Br-Benzo[b]thiophene	n-BuLi, Et <sub>2</sub> O, –20°C	3-Li-Benzo[b]thiophene	199
Cl <sub>4</sub> -Thiophen	n-BuLi, Et <sub>2</sub> O, C <sub>6</sub> H <sub>14</sub> , –25°C	2-Li-3,4,5-Cl <sub>3</sub> -Thiophen	200
2-Br-Pyridine	n-BuLi, Et <sub>2</sub> O, –18°C	2-Li-Pyridine	201
3-Br-Pyridine	n-BuLi, pet ether, –35°C	3-Li-Pyridine	202
2,6-X <sub>2</sub> -Pyridine, X = Br or I	n-BuLi, THF, –90°C	2,6-Li <sub>2</sub> -Pyridine	203
2,6-Br <sub>2</sub> -Pyridine	n-BuLi, Et <sub>2</sub> O, –30°C	2-Li-6-Br-Pyridine	201
3,5-Br <sub>2</sub> -Pyridine	n-BuLi, Et <sub>2</sub> O, –30°C	3-Li-5-Br-Pyridine	201
2-Br-Quinoline	n-BuLi, THF, –60°C	2-Li-Quinoline	204
	2 equiv t-BuLi, THF, –78°C		205

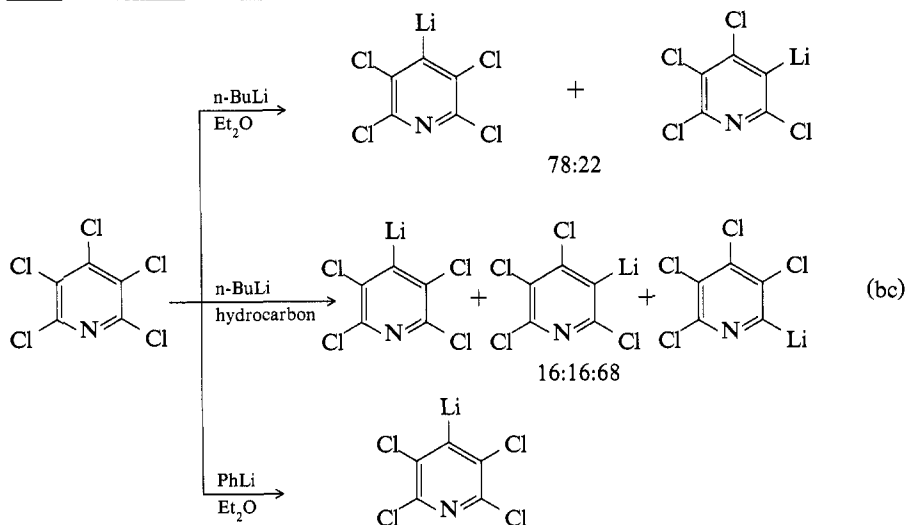
exchanges with 3-Br-pyridine<sup>138</sup>:



i.e., the m-lithio derivative is more stable. The 2,5-Br<sub>2</sub>-pyridine reacts with 1 equiv of n-BuLi in THF at –100°C at the meta position to give 2-Br,5-Li-pyridine<sup>138</sup>. Dilithiation of 2,6-X<sub>2</sub>-pyridine (X = Br or I) can be achieved<sup>203</sup> in THF:



(where X = Br or I); in Et<sub>2</sub>O only one Br group is displaced<sup>201</sup> even with xs n-BuLi; 2,6-di-Cl<sub>2</sub>-pyridine is resistant to Cl–Li exchange. Perhalopyridines react with n-BuLi at the site(s) most susceptible to nucleophilic attack<sup>2</sup>. Reactions between pentachloropyridine and RLi depend on R and the solvent<sup>207,208</sup>.



Pentabromopyridine provides<sup>185</sup>  $p\text{-LiC}_5\text{Br}_4\text{N}$  with  $n\text{-BuLi}$  in  $\text{Et}_2\text{O}$ .

(J. L. WARDLELL)

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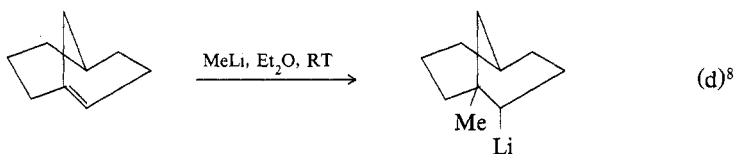


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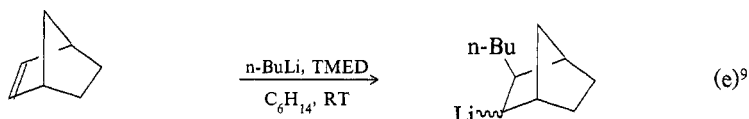
The ratio of **I**:**II** is 98.5:1.5. More allylic deprotonation results from the use of *n*-BuLi-TMED (tetramethylethylenediamine) with  $\text{RCH}_2\text{CH}=\text{CH}_2$ , e.g.,  $\text{R} = \text{H}$  or  $\text{Ph}$  (see §5.5.2.3.2). Ethylene can add to  $\text{PhCH}_2\text{Li}$  in tetrahydrofuran (THF);  $\text{PhCH}_2\text{Li}$  decomposes THF to provide  $\text{CH}_2=\text{CH}_2$ , which then adds to the remaining  $\text{PhCH}_2\text{Li}$  to give  $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{Li}$ . The latter undergoes a 1,3-hydrogen shift to provide<sup>7</sup>  $\text{PhCHLiCH}_2\text{Me}$ .

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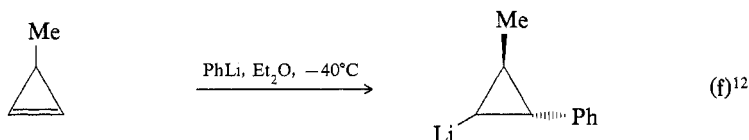
(ii) Additions to Strained Alkenes. Additions to strained alkenes proceed more readily, e.g., with bicyclo[3.3.1]non-1-ene:



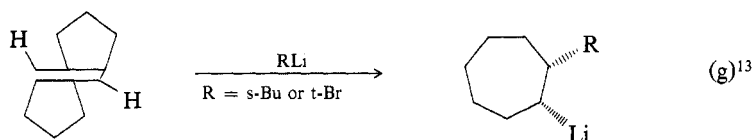
bicyclo[2.2.1]hept-2-ene (norbornene)<sup>9,10</sup>:



benzo[2.2.1]heptadiene<sup>11</sup>, methylcyclopropene<sup>12</sup>:

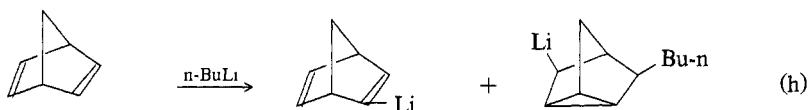


and trans-cyclooctene,<sup>13</sup>



The unstrained cis-cyclooctene, as well as cyclopentene and cyclohexene<sup>10</sup>, are unreactive toward t-BuLi in refluxing petroleum ether. As shown in Eq. (e), n-BuLi adds to norbornene at RT in C<sub>6</sub>H<sub>14</sub> with TMED; t-BuLi adds to norbornene at 60–70°C in petroleum ether, or in refluxing Et<sub>3</sub>N or at 0°C in Et<sub>2</sub>O. The reactivity of trans-octene and norbornene in RLi additions is<sup>13</sup> ca. 17 : 1.

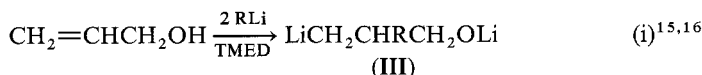
Both addition (with rearrangement) to and metallation of norbornadiene occur<sup>14</sup> with n-BuLi:



(iii) Assisted Additions. A strategically sited internal donor group (OH, OR', NR'<sub>2</sub> or SR') in the alkene can facilitate addition of RLi.

a. Additions to Allylic Alcohols. Allyl alcohol, CH<sub>2</sub>=CHCH<sub>2</sub>OH, reacts with RLi to give LiCH<sub>2</sub>CRHCH<sub>2</sub>OLi in yields dependent on R and the conditions; good yields are

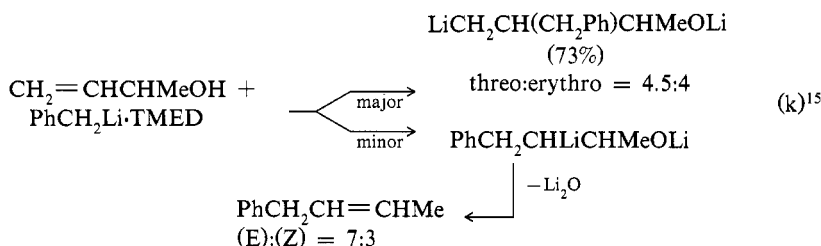
obtained<sup>15–17</sup> with TMED:



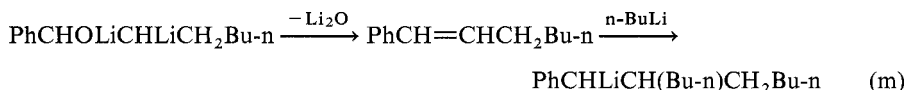
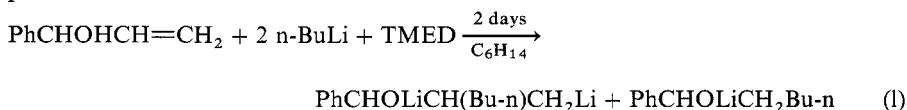
where R = t-Bu, i-Pr, n-Bu, cyclo-C<sub>5</sub>H<sub>11</sub>, Ph or PhCH<sub>2</sub>. The orientation depends on the greater stability of (III) compared to the alternative product, RCH<sub>2</sub>CHLiOLi; such products are unstable. 3-Buten-1-ol reacts similarly with n-BuLi·TMED:



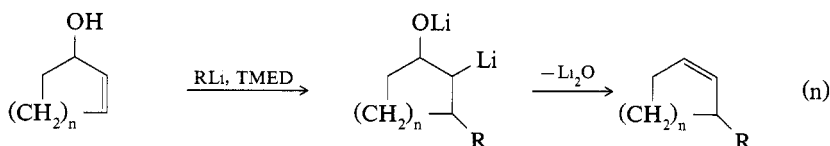
however, with PhCH<sub>2</sub>Li some alkene is also formed from the product of the attack of [PhCH<sub>2</sub>]<sup>−</sup> at the terminal carbon by loss of Li<sub>2</sub>O:



The reaction of PhCH(OH)CH=CH<sub>2</sub> with n-BuLi in C<sub>6</sub>H<sub>14</sub>–TMED provides PhCHOLiCHCH<sub>2</sub>LiBu-n and PhCHLiCH(n-Bu)CH<sub>2</sub>Bu-n in 3:1 ratio. The last product arises from:



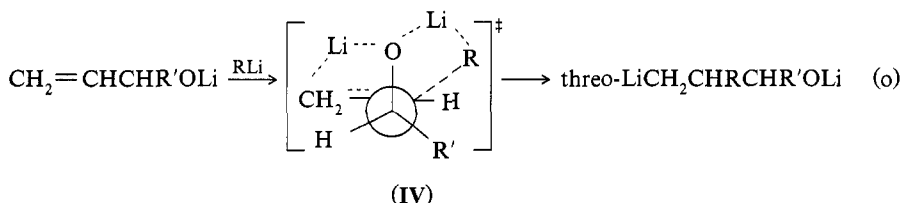
A concerted bond-forming and bond-breaking process<sup>15</sup> is an alternative to Eq. (m). Methylolithium·TMED in C<sub>6</sub>H<sub>14</sub>, or PhLi in THF does not add to PhCHOHCH=CH<sub>2</sub>; t-BuLi adds exclusively at the terminal carbon to form<sup>18</sup> PhCH=CHCH<sub>2</sub>Bu-t and PhCHLiCH(Bu-t)CH<sub>2</sub>Bu-t. Alkene formation is the dominant reaction with 2-cyclopentenol and 2-cyclohexenol:



where n = 1 or 2; R = i-Pr, n-Bu, or t-Bu.

The allylic OH group is vital for the initial addition because neither 3-cyclopentenol nor a mixture of cyclopentene and cyclopentanol reacts<sup>15</sup> with t-BuLi. The importance of the HO group is also seen from the reactions undergone<sup>18</sup> by PhCHOMeCH=CH<sub>2</sub>, including 1,2- and 1,4-rearrangements of the metallated product.

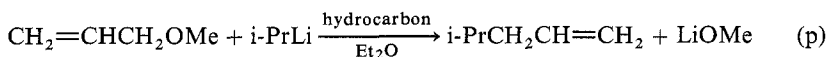
Terminal additions of RLi to  $\text{CH}_2=\text{CHCHROH}$  leads to threeo products and proceeds via transition state **IV** with the attacking RLi coordinated to the OLi group<sup>17,18</sup>:



Reaction of other allylic alcohols with RLi is less selective, with allylic metallations becoming significant, as with<sup>15</sup>  $\text{CH}_2=\text{CMeCH}_2\text{OH}$ . Steric factors and solvents can decide the orientation of the addition and whether allylic metallations occur instead.

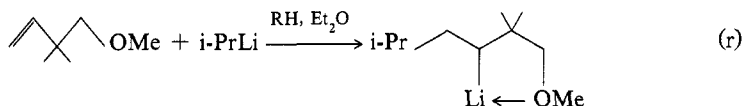
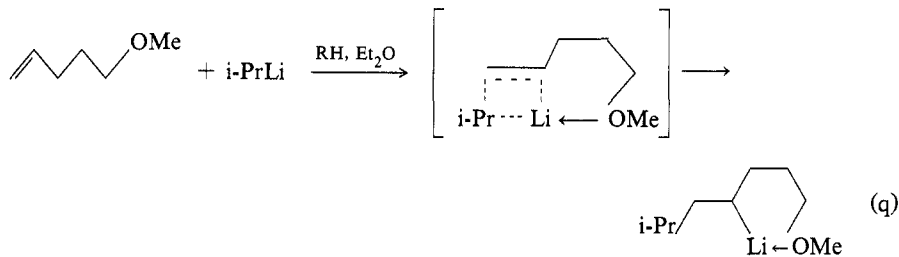
For the metallation of  $\text{CH}_2=\text{CHCH}_2\text{OH}$ , see §5.5.2.3.2.

Reactions of allyl ethers with RLi can lead to replacement of the alkoxy group<sup>20-22</sup>, as shown by allyl methyl ether<sup>20</sup>:

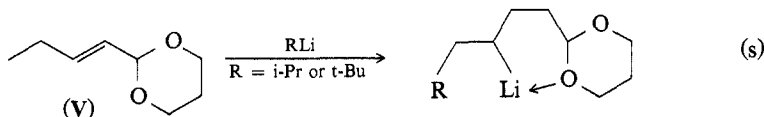


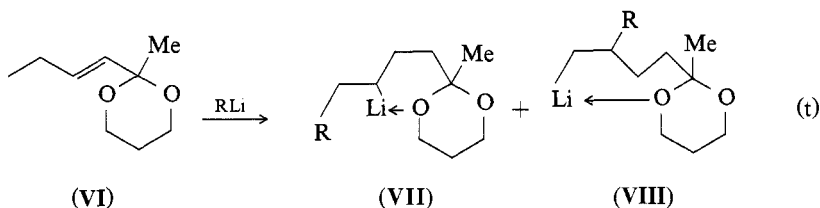
This substitution proceeds<sup>21</sup> with double-bond rearrangement in a cyclic process from a complex of the allyl ether and RLi.

b. Other Alkenyl Alcohols and Ethers. In contrast to  $\text{CH}_2=\text{CHCH}_2\text{OMe}$ ,  $i\text{-PrLi}$  adds regiospecifically<sup>21</sup> to the double bonds in  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{OMe}$  and in  $\text{CH}_2=\text{CHCMe}_2\text{CH}_2\text{OMe}$ . Better yields of the adducts are obtained in mixed  $\text{Et}_2\text{O}$ -hydrocarbon solvents than in the hydrocarbon alone<sup>20</sup>:



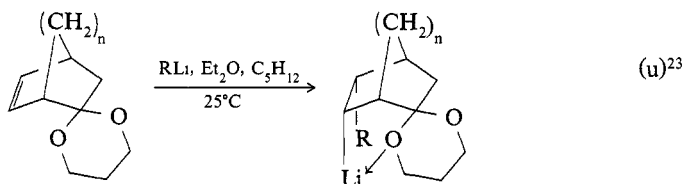
2-Alkenyl-1,3-dioxanes, (**V**) and (**IV**), do not react with primary RLi, such as  $n\text{-BuLi}$ , but do with  $i\text{-PrLi}$  and  $t\text{-BuLi}$ . The additions occur regiospecifically for **V** but not for **VI**:





As well as these addition products, allylic deprotonations also occurs<sup>23</sup>.

Addition to bicyclic alcohols or ethers occurs also<sup>9,20,23,24</sup>, e.g.:



where  $n = 1-3$ ;  $R = n\text{-Bu}$ ,  $i\text{-Pr}$  or  $t\text{-Bu}$ . Coordination of oxygen to Li decides the site of reaction<sup>23</sup>. Some vinyl metallation also results.

Additions of  $n\text{-BuLi}$  to hydroxybicyclo[2.2.1]hept-2-enes indicate the effect an assisting OH group has on the reactivity (see Table 1). These results can be compared to the additions to bicyclo[2.2.1]hept-2-ene. In all cases, the  $n\text{-Bu}$  group is attached at the exo position, but only with endo-bicyclo[2.2.1]hept-5-en-2-ol (**VII**) is the OH group in a position to assist the addition. This leads to enhanced reactivity of **VII** compared to bicyclo[2.2.1]hept-2-ene; the other hydroxy compounds react more slowly. Therefore, a metallated OH group ( $\text{—OLi}$ ) that does not assist addition of  $\text{RLi}$  retards the rate.

In the assisted addition of  $n\text{-BuLi}$  to **VII**, a homoallyl alcohol, the  $n\text{-Bu}$  group is attached to the face of the double bond farther from the hydroxy group—the opposite to the additions of organomagnesium-halide reagents to homoallyl alcohols, and also opposite to the stereochemical findings for additions of  $\text{RLi}$  to allylic alcohols<sup>17</sup>. An  $\text{OLi}$ -assisted addition to syn-bicyclo[2.2.1]hept-2-en-7-ol, **VIII**, would, therefore, lead to the  $n\text{-Bu}$  group's being in the endo position—a reaction that would be unfavored sterically. Hence an unassisted reaction results, with the  $n\text{-Bu}$  group arriving from the more favored exo side. Some metallation also results.

The stereochemistry of the addition of  $i\text{-PrLi}$  to 7- $t\text{-BuO}$ -norbornadiene is exo-cis; exo addition also occurred to syn-7- $t\text{-BuO}$ -norbornene<sup>24</sup>. Additions of  $i\text{-PrLi}$  occur to both endo-5-MeO- and endo-5-MeOCH<sub>2</sub>-bicyclo[2.2.1]hept-2-ene with the  $i\text{-Pr}$  group occupying an exo position in the product<sup>20</sup>. An alternative reaction occurs with exo-5-MeO-bicyclo[2.2.1]hept-2-ene<sup>20</sup>:

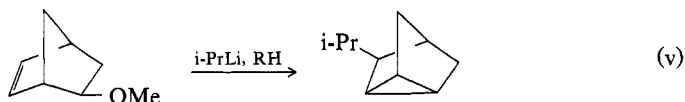

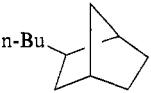
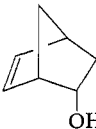
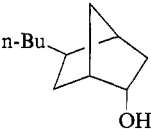
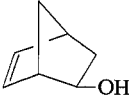
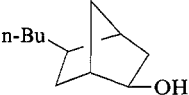
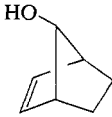
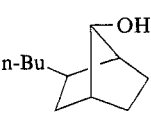
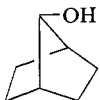
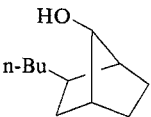


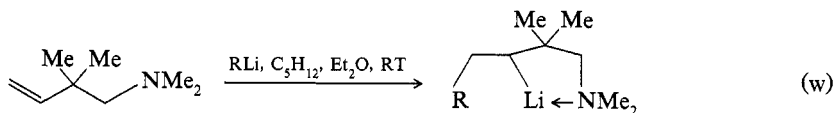
TABLE 1. PRODUCTS OF ADDITION OF n-BuLi TO HYDROXYBICYCLO[2.2.1]HEPT-2-ENES IN THE PRESENCE OF TMED IN C<sub>6</sub>H<sub>14</sub> AT RT AFTER 24 h

Bicyclopheptenol	Product (yield, %) after hydrolysis		
		(30)	1
 VII		(51)	ca. 10 <sup>a</sup>
		(47)	— <sup>b</sup>
 VIII		(26)	<0.1 <sup>b</sup>
		(2)	<0.1 <sup>b</sup>

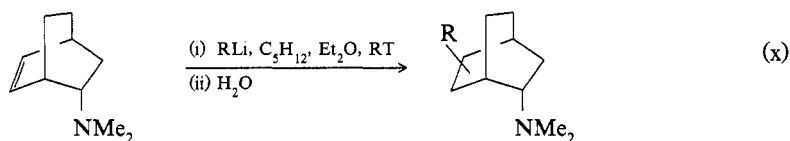
<sup>a</sup> The OLi group assists metallation.

<sup>b</sup> The OLi group does not assist metallation.

c. Alkenyl Amines and Sulfides<sup>25</sup>. In homoallylic acyclic compounds and in suitably orientated cyclic derivatives, these groups enhance the addition reactions:

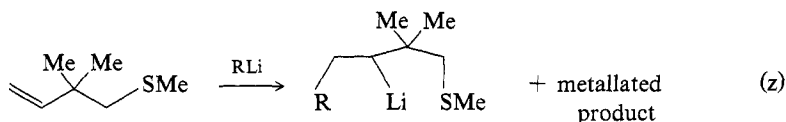
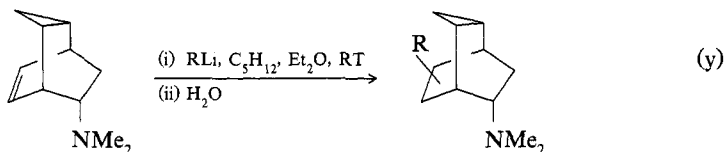


where R = i-Pn or t-Bu;



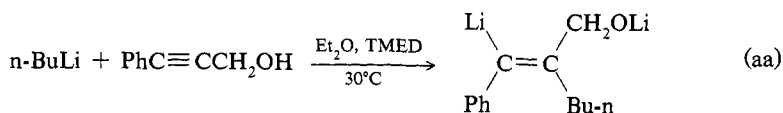


where R = i-Pr, t-Bu or n-Bu (there is no reaction with the anti-isomer);



where R = i-Pr or t-Bu.

(d) Propargylic Alcohols.<sup>26,27</sup> n-Butyllithium adds to propargylic alcohol:



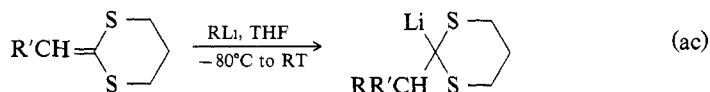
(iv) Addition to  $\alpha$ -Hetero-Substituted Alkenes. Certain  $\alpha$ -hetero-substituted alkenes can undergo addition with RLi, e.g., vinylsilanes, arsines, germanes, phosphines, sulfides and selenides.

Competing reactions to addition to  $\alpha$ -hetero-substituted alkenes are metallation of vinylic or allylic protons (see §5.5.2.3.2) and cleavage of the carbon–hetero-element bond (see §5.5.2.2.1.).  $\alpha$ -Metallations occur with vinylic chlorides, fluorides and ethers; no addition of RLi occurs with vinyl fluorides, chlorides or ethers. For vinylic sulfides and selenides, whether metallation or addition (or even carbon–heterobond cleavage) occurs depends on the conditions and reagents. Addition of RLi (R = Et or n-Bu, not Ph) occurs to aryl vinyl sulfides:

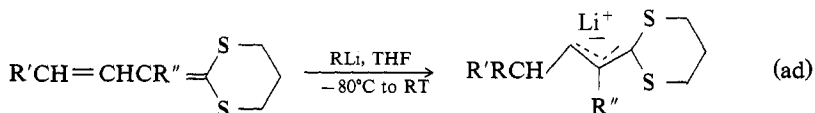


and to<sup>29</sup>  $(\text{CH}_2=\text{CH})_2\text{S}$ . However,  $\alpha$ -metallation of alkyl vinyl sulfides results under similar conditions<sup>28</sup>, or using THF or hexamethylphosphoramide (HMPA) at  $-78^\circ\text{C}$ .

Additions to  $\text{PhSCH=CH}_2$  also can arise in  $\text{Et}_2\text{O}$ –TMED. Methylene 1,3-dithianes can take part in these additions, e.g.<sup>32</sup>:



where if R' = H, R = n-Bu or t-Bu; if R' = Ph, R = t-Bu:



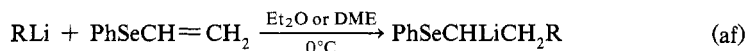
where  $R = n\text{-Bu}$  or  $t\text{-Bu}$ ,  $R' = \text{Me}$ ,  $R'' = \text{H}$ ;  $R' = \text{H}$ ,  $R'' = \text{Me}$ ;  $R', R'' = -(\text{CH}_2)_5-$ , as can<sup>33</sup>  $\text{CH}_2=\text{C}(\text{SiMe}_3)\text{SPh}$ :



where  $R = n\text{-Bu}$  or  $t\text{-Bu}$ .

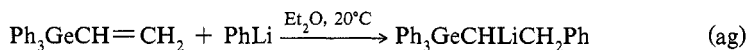
Vinylphenyl selenides can undergo additions<sup>34-36</sup> with  $\text{RLi}$ ,  $\alpha$ -deprotonations (or where possible  $\beta$ -deprotonations) or  $\text{C-Se}$  bond cleavage (see §5.5.2.3.1).

Addition to  $\text{PhSeCH}=\text{CH}_2$  occurs in  $\text{Et}_2\text{O}$  at  $0^\circ\text{C}$  or DME (for  $R = n\text{-Bu}$ ,  $i\text{-Pr}$ ,  $s\text{-Bu}$  or  $t\text{-Bu}$ ); THF is not recommended:

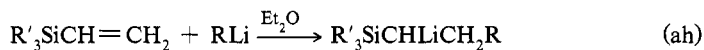


Vinyl bromides or iodides form vinylolithiums with  $\text{RLi}$  instead of adding (see §5.5.2.3.3.).

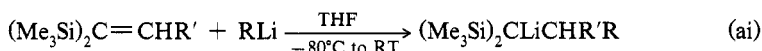
Cleavage of vinyl-Sn and vinyl-Pb bonds with  $\text{RLi}$  gives vinylolithiums (see §5.5.2.3.1.). However, additions<sup>37</sup> result with  $\text{Ph}_3\text{GeCH}=\text{CH}_2$ :



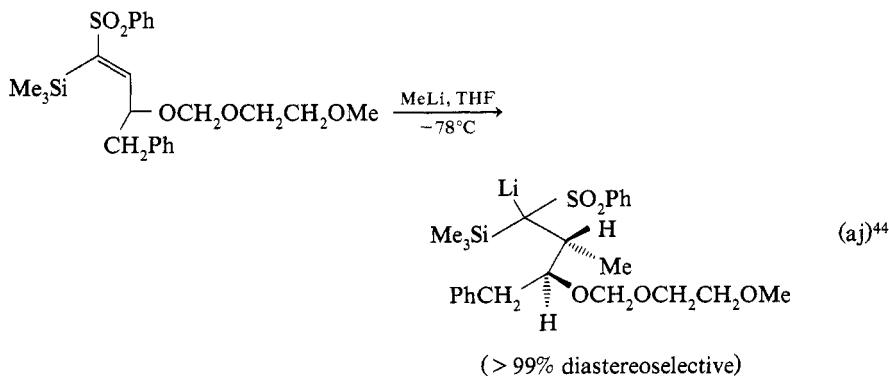
and to vinylsilanes<sup>10,32,38-45</sup>; although cleavage of certain derivatives can occur<sup>46</sup>. Vinylsilanes add to  $\text{R}'_3\text{SiCH}=\text{CH}_2$  ( $R' = \text{Me}$  or  $\text{Ph}$ )<sup>38-41</sup>:



where  $R' = \text{Me}$ ,  $R = t\text{-Bu}$ <sup>10,42</sup>;  $(\text{Me}_3\text{Si})_2\text{C}=\text{CHR}'$ <sup>32</sup>:

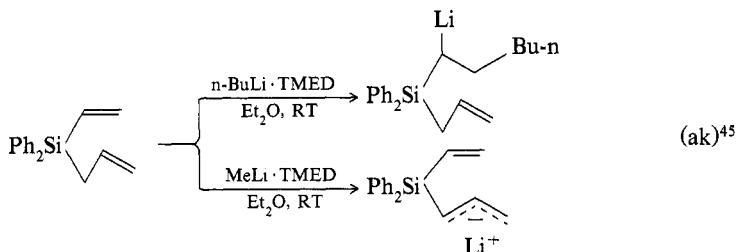


where if  $R' = \text{H}$ ,  $R'' = n\text{-Bu}$ ,  $i\text{-Bu}$  or  $t\text{-Bu}$ , and if  $R' = \text{Ph}$ ,  $R = t\text{-Bu}$  ( $\text{MeLi}$  or  $\text{PhLi}$  are unreactive);  $\text{Me}_3\text{Si}(\text{PhS})\text{C}=\text{CH}_2$ <sup>40</sup>,  $\text{Me}_3\text{Si}(\text{PhSO}_2)\text{C}=\text{CHR}$ <sup>40,44</sup>:

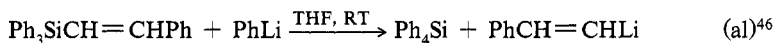


$\text{Ph}_3\text{SiCPh}=\text{CH}_2$ <sup>40</sup> and to  $\text{Et}_3\text{SiCF}=\text{CF}_2$  (using  $\text{RLi}$  with  $R = \text{Ph}$ ,  $\text{CH}_2=\text{CH}$ ,  $\text{CH}_2=\text{CHCH}_2$  or  $n\text{-Bu}$ ). The high stereoselectivity in Eq: (aj) arises from the coordination of  $\text{MeLi}$  by the  $\text{OCH}_2\text{OCH}_2\text{CH}_2\text{OMe}$  group.

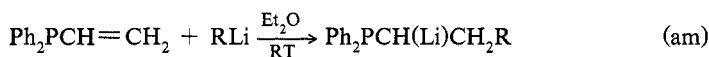
By changing the lithiating agent, either of the two unsaturated groups in  $\text{Ph}_2\text{Si}(\text{CH}=\text{CH}_2)\text{CH}_2\text{CH}=\text{CH}_2$  can be brought into reaction:



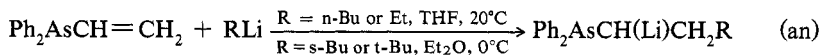
By suitable substitution, cleavage of vinyl-Si bonds can result:



Cleavage also results in reactions<sup>47</sup> of  $n\text{-BuLi}$  and  $\text{Ph}_3\text{SiC}\equiv\text{CR}$ . Additions also occur<sup>48</sup> to other vinyl-metal or -metalloidal species, such as  $\text{Ph}_2\text{PCH}=\text{CH}_2$ :

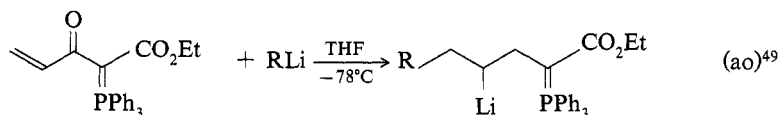


where  $\text{R} = n\text{-Bu}$  or  $t\text{-Bu}$ , or  $\text{Ph}_2\text{AsCH}=\text{CH}_2$ <sup>34</sup>:




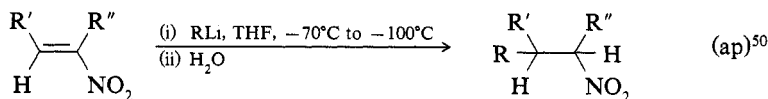
Telomerization occurs<sup>48</sup> using  $n\text{-Bu}_2\text{PCH}=\text{CH}_2$ .

Various  $\text{RLi}$  add<sup>49</sup> to the ylide,  $\text{CH}_2=\text{CHCOC}(=\text{PPh}_3)\text{CO}_2\text{Et}$ :



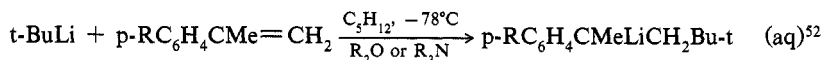
where  $\text{R} = \text{Me}$ ,  $\text{CH}_2=\text{CH}$ ,  $\text{CH}_2=\text{COMe}$ ,  $t\text{-BuOCOCH}_2$ ,  $\text{Me}_3\text{SiC}\equiv\text{CCH}_2$ , or

, but not  $\text{MeC}\equiv\text{C}$ . Nitroalkenes also undergo addition, e.g.<sup>50</sup>:

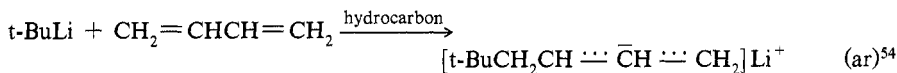


where, e.g.,  $\text{R} = \text{Ph}$ ;  $\text{R}' = \text{H}$  or  $\text{Ar}$ ;  $\text{R}'' = \text{H}$  or  $\text{Me}$ ;

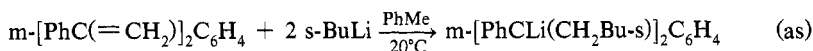
(v) Additions to Conjugated Alkenes and Alkynes. Addition to carbon-carbon multiple bonds occur more readily than to isolated bonds; polymerization may result<sup>1,5</sup>, as with  $\text{PhCH}=\text{CH}_2$ ,  $\text{CH}_2=\text{CHCH}=\text{CH}_2$  and  $\text{CH}_2=\text{CMeCH}=\text{CH}_2$ . Under controlled conditions, e.g., at low  $T$ , and with hindered systems, monoaddition products can be obtained, even with<sup>51-53</sup>, e.g.,  $\text{ArCR}=\text{CH}_2$ :



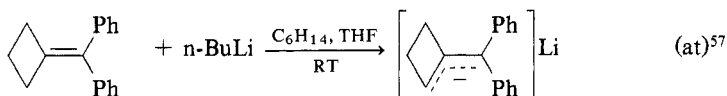
And 1,3-butadienes<sup>54,55</sup>:



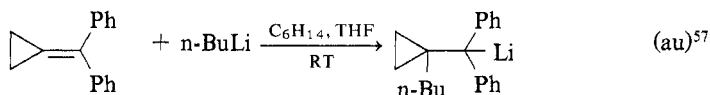
Additions to both olefinic bonds in  $m\text{-(H}_2\text{C}=\text{CPh)}_2\text{C}_6\text{H}_4$  occur<sup>56</sup>:



Metallation at adjacent acidic sites may occur as a minor or major component, e.g.:

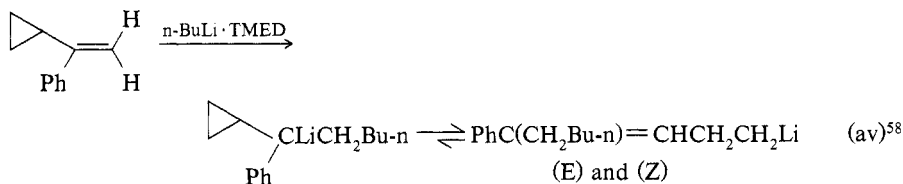


In contrast, addition occurs to the cyclopropyl analogue:

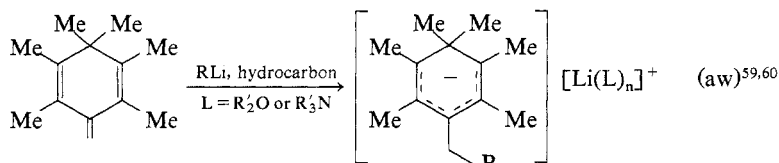


The difference results from the greater ease of introducing a further  $\text{sp}^2$  center in the four- as compared to the three-membered ring.

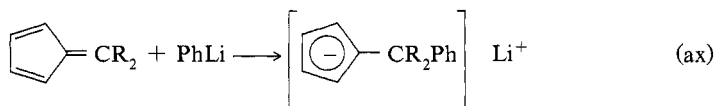
Addition, followed by isomerization, results in the reaction of 1-Ph-1-cyclo- $\text{C}_3\text{H}_5\text{C}=\text{CH}_2$ :



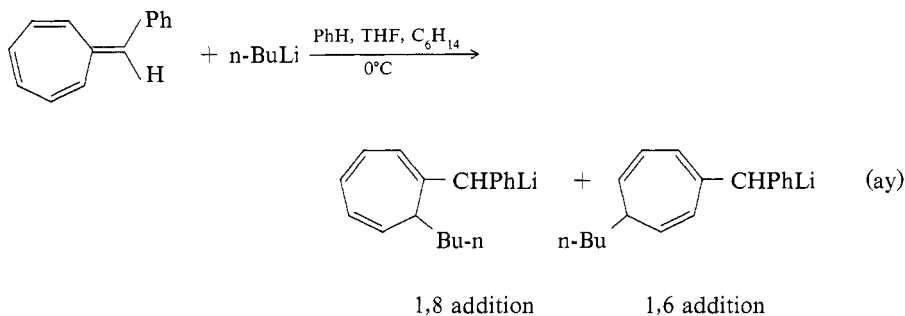
1-Methylene-2,5-cyclohexadienes also undergo additions<sup>59,60</sup>:



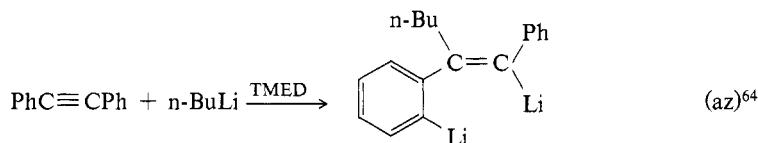
as do fulvenes<sup>61-62</sup>, including heptafulvenes<sup>63</sup>:



where  $R_2 = \text{Me}_2, \text{Ph}_2$  or  $-(\text{CH}_2)_5-$ ;

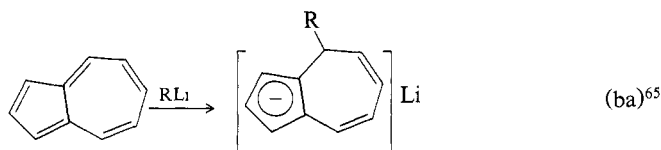


Organolithiums also add to diarylacetylenes, especially if TMED is also present. Under these conditions ortho-metallation occurs as well as addition<sup>64</sup>:

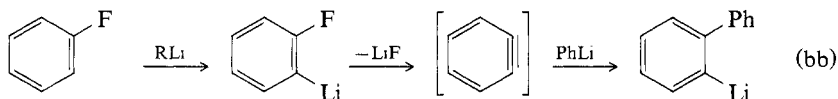


Metallations result with  $\text{RC}\equiv\text{CH}$  or with  $\text{RCH}_2\text{C}\equiv\text{CR}'$  (see §5.5.2.3.2).

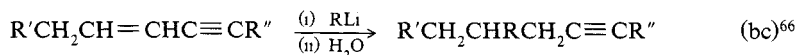
Alkylolithiums add to arenes, e.g., naphthalenes; however, as  $\text{LiH}$  is lost from the adduct, the overall reaction is alkylation<sup>1</sup>. Adducts from azulene are obtained in good yields:



Also  $\text{RLi}$  adds to arynes<sup>1</sup>:

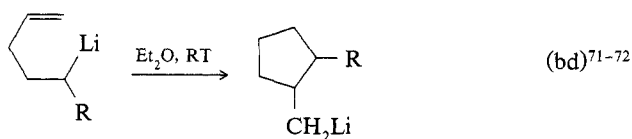


The addition of organolithiums to conjugated enynes occurs to the double bond<sup>66–70</sup>:

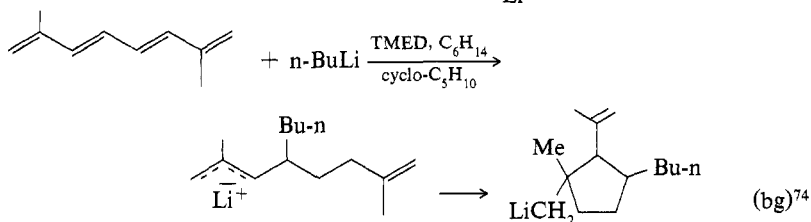
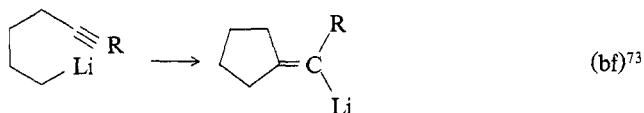
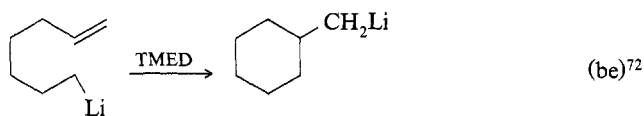


where  $\text{R} = \text{allyl or } n\text{-Bu}$ ;  $\text{R}' = \text{alkyl, OH, OBU-n, NHEt or NEt}_2$ ;  $\text{R}'' = \text{H or Me}$ .

(vi) Intramolecular Additions. Intramolecular additions with both alkenyl- and alkynyllithiums occur under milder conditions than required for intermolecular addition, e.g.:

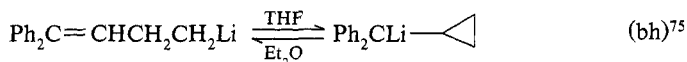


The reaction is faster in Et<sub>2</sub>O than in PhH or cyclopentane.

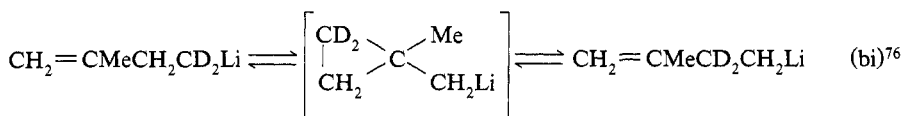


The smaller of the two possible rings is obtained.

Equilibria may exist also:

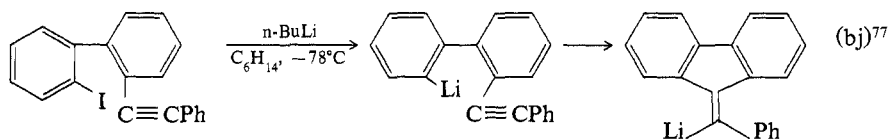


The open-chain compound is favored in Et<sub>2</sub>O, whereas the cyclopropylmethyl form is stable<sup>75</sup> in THF. Reversible behavior can be detected by isotopic labeling, e.g.:

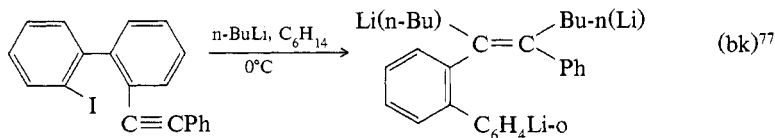


Only the acyclic species are present in solution.

A diarylacetylene adds intramolecularly:



At 0°C, both concurrent Li—I exchange and addition to the triple bond occur with no cyclization resulting:



(J. L. WARDELL)

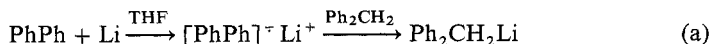
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(i) **Metallations.** The compound  $[\text{PhPh}]^\cdot\text{Li}^+$  in tetrahydrofuran (THF) reacts with  $\text{Ph}_3\text{CH}$  quantitatively, and with  $\text{Ph}_2\text{CH}_2$  (ca. 50% metallation). Less than 1% metallation occurs with  $\text{PhMe}$  under similar conditions<sup>5</sup>:



Compounds require a  $\text{pK}_a < 35$  to react with  $[\text{PhPh}]^\cdot\text{Li}^+$ .

Dianions,  $[\text{ArH}]^{2-}\text{Li}^+$  ( $\text{ArH}$  = naphthalene, anthracene or  $\text{PhPh}$ ), with  $\text{Ph}_3\text{CH}$  and  $\text{Ph}_2\text{CH}_2$  also give  $\text{Ph}_3\text{CLi}$  and  $\text{Ph}_2\text{CHLi}$ , respectively, and are more reactive than the radical anions. Metallation<sup>6</sup> by  $[\text{ArH}]^{2-}\text{Li}^+$  is faster in THF than in  $\text{Et}_2\text{O}$ .

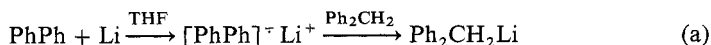


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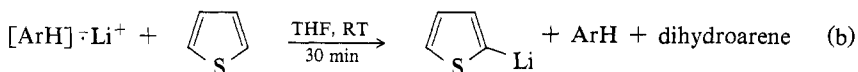


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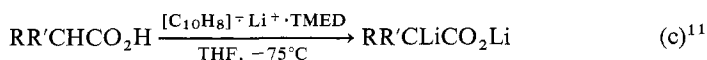
Contact ion-paired  $[\text{ArH}]^{\cdot-} \text{M}^+$  is more reactive than the solvent-separated ion-paired form; i.e., the rate of metallations using  $[\text{anthracene}]^{\cdot-} \text{M}^+$  increases as the donor ability of the solvent decreases<sup>7</sup>.

Thiophene is metallated<sup>8</sup> by  $[\text{ArH}]^{\cdot-} \text{Li}^+$  in THF:



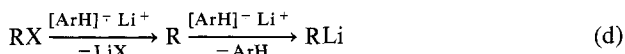
The yield of metallated thiophene is ca. 50% when ArH is naphthalene. The reactivity of ArH is:  $\text{ArH} = \text{PhPh} > \text{naphthalene} > \text{PhCH}=\text{CHPh} > \text{phenanthrene} > \text{anthracene}$ . The normal two-electron reaction using  $[\text{ArH}]^{\cdot-} \text{Li}^+$  changes to a one-electron process in the presence of  $\text{Ph}_2\text{C}=\text{CH}_2$  or  $\text{PhCMe}=\text{CH}_2$ , and yields of 2-thienyl-Li also increase to >90%.

Lithiation of functional substituted alkanes is also achieved in these electron transfers, e.g., of  $\text{RCH}_2\text{CN}$  ( $\text{R} = \text{Ph}$  or  $\text{H}$ )<sup>9</sup> by  $[\text{naphthalene}]^{2-} \text{Li}^+$  and of  $\text{RR}'\text{-CHCO}_2\text{H}$ <sup>10,11</sup> by  $[\text{naphthalene}]^{\cdot-} \text{Li}^+$ :



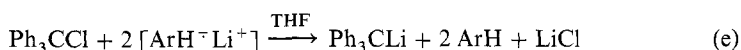
where  $\text{R}, \text{R}' = \text{Me}, \text{Me}; \text{Ph}, \text{H}; \text{Me}, \text{H}; -(\text{CH}_2)_5-$ .  $[\text{Naphthalene}]^{\cdot-} \text{Li}^+$  is of equal reactivity to  $\text{LiN}(\text{Pr-}i)_2$ , but use of  $[\text{C}_{10}\text{H}_8]^{\cdot-} \text{Li}^+$  is preferred because its reaction product,  $\text{C}_{10}\text{H}_8$ , has no nucleophilicity, unlike  $\text{HN}(\text{Pr-}i)_2$  formed from  $\text{LiN}(\text{Pr-}i)_2$ .

(ii) Reactions of Organic Halides. Two equivalents of  $[\text{ArH}]^{\cdot-} \text{Li}^+$  are required to give organolithiums:



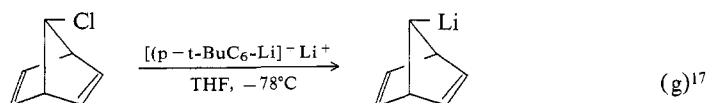
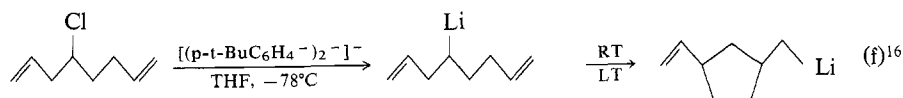
where  $\text{X} = \text{F}, \text{Cl}$  or  $\text{Br}$ . No  $\text{RLi}$  is obtained with only 1 equiv of  $[\text{ArH}]^{\cdot-} \text{Li}^+$ . Alkylation to give alkyldihydroaromatic compounds is a side reaction.

Reactions occur with alkyl halides; e.g.,  $\text{Ph}_3\text{CCl}$  undergoes  $\text{Cl-Li}$  exchange<sup>12</sup> in THF with  $[\text{phenanthrene}]^{\cdot-} \text{Li}^+$  at  $25^\circ\text{C}$  or with<sup>13</sup>  $[\text{naphthalene}]^{\cdot-} \text{Li}^+$ :



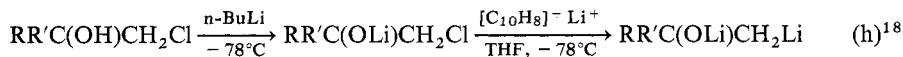
The  $\{[\text{p-t-Bu-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Bu-t-p}]^{\cdot-} \text{Li}^+\}$  is more effective<sup>14,15</sup> as a lithiating agent than either  $[\text{C}_{10}\text{H}_8]^{\cdot-} \text{Li}^+$  or  $[2,7\text{-di-(t-Bu)}_2\text{naphthalene}]^{\cdot-} \text{Li}^+$ , giving 90% yields of  $\text{RLi}$  from  $\text{RX}$  ( $\text{RX} = \text{p- or s-alkyl halide}$ ) in THF, because the bulky t-Bu groups and the higher reduction potential prevent coupling.

The 4-Li-1,7-octadiene and 7-Li-norbornadiene are prepared using  $[\text{p-t-BuC}_6\text{H}_4\text{-C}_6\text{H}_4\text{Bu-t-p}]^{\cdot-} \text{Li}^+$  under mild conditions:



where  $R=H$ ,  $R'=Me$ ,  $i-Pr$ ,  $Ph$  or  $PhCH_2$ . syn-7-Bromo-norbornene reacts to give a mixture of syn- and anti-7-Li-norbornene<sup>17</sup>.

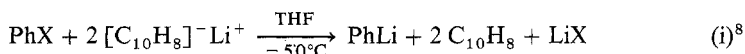
A step involving an organic chloride with  $[C_{10}H_8]^- Li^+$  is incorporated into a synthesis of  $\beta$ -alkoxyalkyllithiums<sup>18,19</sup>:



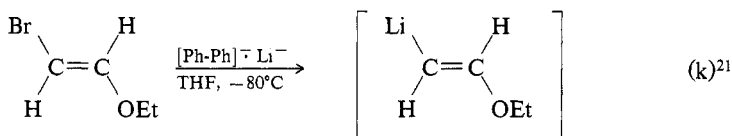
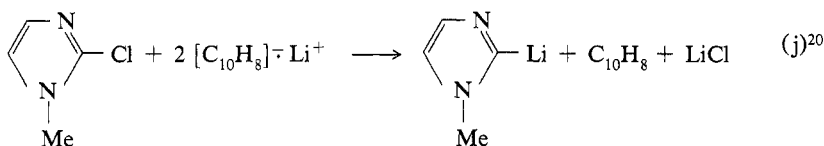
where  $R = H$ ,  $R' = Me$ ,  $i-Pr$ ,  $Ph$  or  $PhCH_2$ .

The reaction of  $[C_{10}H_8]^{2-} Li^+$  in  $Et_2O$  with  $C_6H_{13}CHMeBr$  gives only 9% electron transfer against 57% for  $[C_{10}H_8]^- Li^+$  in THF. Similarly  $[p-t-Bu_2naphthalene]^{2-} 2 Li^+$  gives 34% electron transfer in  $Et_2O$  vs. 96% for  $[p-t-Bu_2C_{10}H_6]^- Li^+$  in THF. These results<sup>14</sup> and others<sup>17</sup> suggest that solvent-separated ion pairs give more electron transfer than contact ion pairs of  $[ArH]^- Li^+$ , which in turn give more electron transfer than the contact ion triplets of  $[ArH]^{2-} Li^+$ . Therefore, polar solvents are best for formation of  $RLi$  from  $RX$ .

Aryl and vinyl halides also undergo halogen-lithium exchanges with  $[ArH]^- Li^+$ :



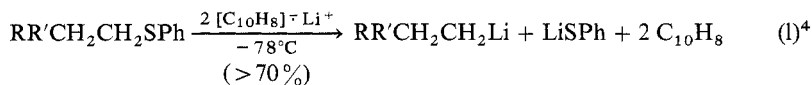
where  $X = F$  or  $Cl$ ;



In contrast to Eq. (k), metallation occurs with  $n-BuLi$  at  $-80^\circ C$  to give (Z)- $CBrLi = CHOEt$ .

Free radicals,  $R'$ , are formed in these reactions; only if  $R'$  could be trapped before any isomerization occurs would the stereochemistry of the organic halide be retained. The equilibration of radicals proceeds at a faster rate than reaction of  $R'$  with  $[ArH]^- Li^+$  to give  $RLi$ . The ratios of organo-Li products reflect the equilibrium ratios of the intermediate free radicals<sup>17,22,23</sup>. Table 1 provides further examples.

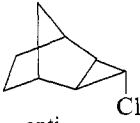
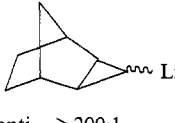
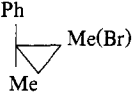
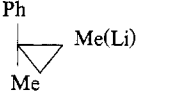
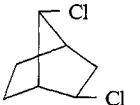
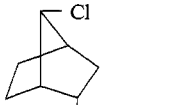
(iii) Reaction of Organic Sulfides. Organic sulfides are cleaved by  $[ArH]^- Li^+$ , e.g.:



As  $RR'CH_2CH_2SPh$  is formed from  $RR'C=CH_2$  with  $HSPh$ , the overall conversion is from  $RR'C=CH_2$  to  $RR'CHCH_2Li$ .

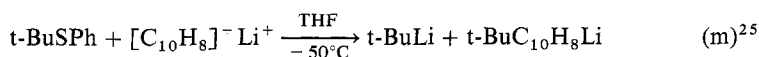
As shown by  $PhS(CH_2)_nCl$ ,  $Cl$  is more reactive than the  $PhS$  group toward  $[C_{10}H_8]^- Li^+$ ; reaction of  $PhS(CH_2)_nCl$  ( $n = 3, 4, 5, 6$ ), therefore, leads<sup>4</sup> to  $Ph(CH_2)_nLi$ .

TABLE 1. FORMATION OF ORGANOLITHIUMS VIA REACTION OF ORGANIC HALIDES WITH LITHIUM ARENE RADICAL ANIONS IN THF

Organic halide	Lithiating agent <sup>a</sup>	Product (yield, %)	Ref.
n-BuCl	[phen] <sup>•-</sup> Li <sup>+</sup> , -100°C	n-BuLi	8
Ph <sub>2</sub> CHCl	[phen] <sup>•-</sup> Li <sup>+</sup> , -50°C	Ph <sub>2</sub> CHLi	8
cyclo-C <sub>6</sub> H <sub>11</sub> Cl	[C <sub>10</sub> H <sub>8</sub> ] <sup>•-</sup> Li <sup>+</sup> , -50°C	cyclo-C <sub>6</sub> H <sub>11</sub> Li	8
PhCl	[C <sub>10</sub> H <sub>8</sub> ] <sup>•-</sup> Li <sup>+</sup> , -50°C	PhLi	8
PhF	[C <sub>10</sub> H <sub>8</sub> ] <sup>•-</sup> Li <sup>+</sup> , -50°C	PhLi	8
C <sub>8</sub> H <sub>17</sub> Cl	Li·DBB, THF, -78°C	n-C <sub>8</sub> H <sub>17</sub> Li (94)	14
C <sub>8</sub> H <sub>17</sub> Br	Li·DBB, THF, -78°C	n-C <sub>8</sub> H <sub>17</sub> Li (91)	14
C <sub>6</sub> H <sub>13</sub> CHMeCl	Li·DBB, THF, -78°C	n-C <sub>6</sub> H <sub>13</sub> CHMeLi (87)	14
n-BuCMeEtCl	Li·DBB, THF, -78°C	n-BuCMeEtLi (88)	14
7-Chloro-norcarane	Li·DBB, THF, -78°C	7-Li-Norcarane (95)	14
2(4)-Chlorosemibulvalene	Li·DBB, THF, -78°C	2(4)-Li-semibulvalene	24
	Li·DBB, THF, -78°C		22
anti Ph 	[C <sub>10</sub> H <sub>8</sub> ] <sup>•-</sup> Li <sup>+</sup> , THF, 20°C	syn:anti = > 200:1 Ph 	23
Me either isomer 	Li·DBB, THF, -78°C	trans:cis 45:55 	24
		Li	

<sup>a</sup> Phen = phenanthrene; Li·DBB = [p-t-BuC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Bu-t-p]<sup>•-</sup> Li<sup>+</sup>.

The reactions of s- or t-alkyl phenyl sulfides by [C<sub>10</sub>H<sub>8</sub>]<sup>•-</sup> Li<sup>+</sup> produce alkyl-Li as well as lithiated alkylidihydronaphthalenes<sup>25</sup>, e.g.:



Benzylic aryl sulfides work well:



α-Alkoxyalkyllithiums are obtained from α-PhS-substituted ethers<sup>21</sup>:

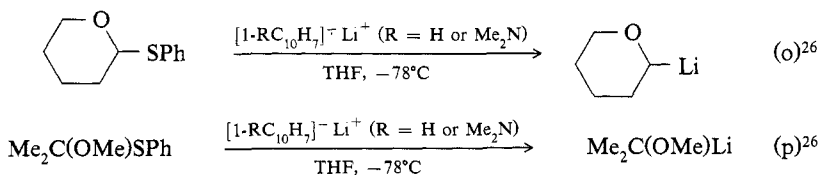
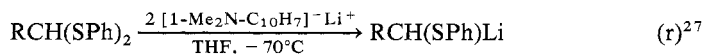
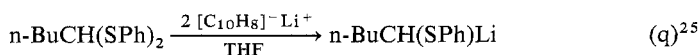


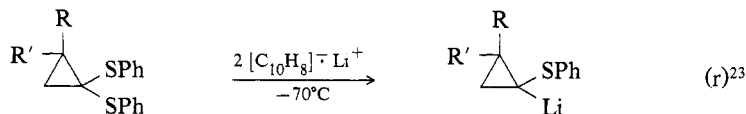
TABLE 2. FORMATION OF ORGANOLITHIUMS FROM ARYL SULFIDES AND LITHIUM NAPHTHALENE RADICAL ANIONS

Sulfide	Lithiating conditions	Product	Refs.
cyclo-C <sub>6</sub> H <sub>11</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	cyclo-C <sub>6</sub> H <sub>11</sub> Li	25
PhSCH(Ph)(CH <sub>2</sub> ) <sub>n</sub> CHPh(SPh)	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	LiCHPh(CH <sub>2</sub> ) <sub>n</sub> CHPhLi	25
n = 3–5, or 10			
PhRC(OH)CH(Ph)SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	PhRC(OLi)CH(Ph)Li	25
R = Ph or Me			
Ph <sub>2</sub> CSPPhCMeHEt	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –65°C	Ph <sub>2</sub> CLiCHMeEt	
C <sub>7</sub> H <sub>15</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	C <sub>7</sub> H <sub>15</sub> Li	4
Ph(CH <sub>2</sub> ) <sub>4</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	Ph(CH <sub>2</sub> ) <sub>4</sub> Li	4
p-(PhSCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	p-(LiCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4
O(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SPh) <sub>2</sub>	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	O(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Li) <sub>2</sub>	4
PhO(CH <sub>2</sub> ) <sub>4</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	PhO(CH <sub>2</sub> ) <sub>4</sub> Li	4
PhS(CH <sub>2</sub> ) <sub>n</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	PhS(CH <sub>2</sub> ) <sub>n</sub> Li	4
n = 2, 4, 5 or 6			
Cl(CH <sub>2</sub> ) <sub>n</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF	PhS(CH <sub>2</sub> ) <sub>n</sub> Li	4
n = 3–6			
PrCH(OMe)SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	PrCH(OMe)Li	26
OCMe = CH(CH <sub>2</sub> ) <sub>2</sub> CHSPh	[1-Me <sub>2</sub> NC <sub>10</sub> H <sub>7</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	OCMe = CH(CH <sub>2</sub> ) <sub>2</sub> CHLi	26
CH <sub>2</sub> CH <sub>2</sub> C(OMe)SPh	[1-Me <sub>2</sub> NC <sub>10</sub> H <sub>7</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	CH <sub>2</sub> CH <sub>2</sub> C(OMe)Li	26
PhSCH <sub>2</sub> CH = CMe(OSiMe <sub>3</sub> )	[1-Me <sub>2</sub> NC <sub>10</sub> H <sub>7</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	LiCH <sub>2</sub> CH = CMe(OSiMe <sub>3</sub> )	26
CH <sub>2</sub> CH <sub>2</sub> C(SPh) <sub>2</sub>	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –70°C	CH <sub>2</sub> CH <sub>2</sub> CCLiSPh	28
CH <sub>2</sub> CMe <sub>2</sub> C(SPh) <sub>2</sub>	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –70°C	CH <sub>2</sub> CMe <sub>2</sub> CLiSPh	28
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> C = C(SPh) <sub>2</sub>	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –70°C	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> C = CLiSPh	29
Me <sub>2</sub> C = C(SPh) <sub>2</sub>	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –70°C	Me <sub>2</sub> C = CLiSPh	29
EtCH(SPh) <sub>2</sub>	[1-Me <sub>2</sub> NC <sub>10</sub> H <sub>7</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	EtCH(SPh)Li	30
EtCH(SPh)SiMe <sub>3</sub>	[1-Me <sub>2</sub> NC <sub>10</sub> H <sub>7</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	EtCH(SiMe <sub>3</sub> )Li	30
HC(SiMe <sub>3</sub> ) <sub>3</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –78°C	HC(SiMe <sub>3</sub> ) <sub>3</sub> Li	31
PhCMe <sub>2</sub> SPh	[C <sub>10</sub> H <sub>8</sub> ] <sup>·-</sup> Li <sup>+</sup> , THF, –60°C	PhCMe <sub>2</sub> Li	32

Because  $\alpha$ -alkoxyalkyllithiums are difficult to obtain by other methods, this route is valuable. An advantage of using [1-Me<sub>2</sub>NC<sub>10</sub>H<sub>7</sub>]<sup>·-</sup> Li<sup>+</sup> is the easier separation of 1-Me<sub>2</sub>NC<sub>10</sub>H<sub>7</sub> from the reaction mixture than C<sub>10</sub>H<sub>8</sub>.

Gem-diphenyl sulfides undergo cleavage with 2 equiv of [C<sub>10</sub>H<sub>8</sub>]<sup>·-</sup> Li<sup>+</sup> to provide  $\alpha$ -PhS-alkyl-Li, e.g.:





where R, R' = Me, H; R = R' = H, Me.

Ketene bis(phenylthio)acetals also are reactive toward  $[\text{C}_{10}\text{H}_8]^\cdot \text{Li}^+$ :



where R, R' = cyclo- $\text{C}_6\text{H}_{11}$ , H; Me, Me;  $-(\text{CH}_2)_5-$ .

This route leads to  $\alpha$ -PhS-vinylolithiums; attempts to prepare these compounds by deprotonation of  $\text{RR}'\text{C} = \text{CHSPh}$  with *s*-BuLi, THF-HMPA at 78°C fail.

Table 2 provides further examples.

(J. L. WARDELL)

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### 5.5.3. Carbon–Group-IA Bonds

#### 5.5.3.1. from the Elements

The group-IA elements react with carbon to give either  $M_2C_2$  acetylides or liq  $H_2O$  or its vapor giving acetylene from the carbides and  $H_2$  from the intercalates. to a  $C\equiv C$  group, while the intercalation compounds form when metal atoms occupy positions between the hexagonal sheets in graphite. These compounds are reactive to  $H_2O$  liquid or its vapor giving acetylene from the carbides and  $H_2$  from the intercalates. Consequently, **there is a risk of a gas explosion when handling these materials in the presence of moisture.** The group IB elements form explosive acetylides.

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##### 5.5.3.1.1. Giving Na Carbides.

The carbide  $Na_2C_2$  cannot be prepared by direct reaction between Na metal and carbon. However, acetylene will react directly with metallic Na at  $400^\circ\text{--}600^\circ\text{C}$  or with Na in  $NH_3$  to give the carbide. At lower T, the unstable  $NaC_2H$  will form which can be decomposed at  $200^\circ\text{C}$  to give the carbide. The carbide is unstable at  $>800^\circ\text{C}$ . Instead of Na,  $NaNH_2$  can be dissolved in liq  $NH_3$  to give a more efficient conversion<sup>1</sup>.

A deep-violet, stage VIII intercalation compound exists with a stoichiometry  $NaC_{64}$ <sup>2</sup>. This can be formed by heating a mixture of powdered graphite containing ca. 3 wt % Na at  $120^\circ\text{--}500^\circ\text{C}$ <sup>3</sup>. Although the graphite must be free of oxygen to prevent the formation of  $Na_2CO_3$ , a little oxygen accelerates the reaction<sup>3</sup>.

Sodium vapor attacks graphite at  $500^\circ\text{--}750^\circ\text{C}$  to give  $NaC_{64}$ , especially if liq Na is present<sup>2,4</sup>.

Pure  $NaC_{64}$  is prepared by encapsulating graphite in soda glass and making this an electrode in a bath of  $NaNO_2$  held at  $400^\circ\text{C}$ . The transport of  $Na^+$  through the glass results in a controlled amount of pure liq Na within the glass container<sup>3,5</sup>. The reaction proceeds to completion at  $400^\circ\text{C}$ .

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##### 5.5.3.1.2. Giving K, Rb and Cs Carbides.

The carbides of these elements can be prepared by reacting either the metals or a solution of the metals in liq  $NH_3$  with acetylene. The resulting acetylide can be decomposed to give the carbide by rapid heating in vacuum to  $300^\circ\text{C}$ <sup>1–3</sup>.

Graphite reacts with the molten metals or their vapors to give  $MC_8$  (bronze or copper red),  $MC_{24}$  (steel blue),  $MC_{36}$ ,  $MC_{48}$ , and  $MC_{60}$ <sup>4,6</sup>. A range of composition is

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A deep-violet, stage VIII intercalation compound exists with a stoichiometry  $NaC_{64}$ <sup>2</sup>. This can be formed by heating a mixture of powdered graphite containing ca. 3 wt% Na at 120°–500°C<sup>3</sup>. Although the graphite must be free of oxygen to prevent the formation of  $Na_2CO_3$ , a little oxygen accelerates the reaction<sup>3</sup>.

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##### 5.5.3.1.2. Giving K, Rb and Cs Carbides.

The carbides of these elements can be prepared by reacting either the metals or a solution of the metals in liq  $NH_3$  with acetylene. The resulting acetylide can be decomposed to give the carbide by rapid heating in vacuum to 300°C<sup>1–3</sup>.

Graphite reacts with the molten metals or their vapors to give  $MC_8$  (bronze or copper red),  $MC_{24}$  (steel blue),  $MC_{36}$ ,  $MC_{48}$ , and  $MC_{60}$ <sup>4,6</sup>. A range of composition is

possible at each stage owing to metal atom vacancies or to a nonuniform spacing of the metal layers.

(E. K. STORMS)

1. H. Moissan, *C.R. Hebd. Seances Acad. Sci.*, **126**, 303 (1898).
2. H. Moissan, *C.R. Hebd. Seances Acad. Sci.*, **136**, 1221 (1903).
3. K. Fredenhagen, G. Cadenbach, *Z. Anorg. Allg. Chem.*, **158**, 249 (1926).
4. M. A. M. Boersma, *Catal. Rev. Sci. Eng.*, **10**, 243 (1974).
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6. T. J. Salzano, S. Aronson, *J. Inorg. Nucl. Chem.*, **26**, 1456 (1964).

### 5.5.3.2. from the Group-IA Metals and Their Alloys

#### 5.5.3.2.1. with Organic Halides.

The reaction of organic halides with alkali metals:



yields organoalkali compounds, e.g.,  $n\text{-C}_5\text{H}_{11}\text{Na}$ , under proper experimental conditions. Contact must be effected between the metal and the organic halide because unless reaction (a) is rapid, the organoalkali is destroyed by reaction with unreacted alkyl halide to give products of coupling and  $\alpha$ , and  $\beta$ , elimination (olefin and alkane). To retard such side reactions, organic chlorides are used in preference to bromides and iodides<sup>1</sup>.

Good contact between alkali metal and organic chloride can be effected using a sand or dispersion formed by stirring the molten metal under an inert solvent, such as *n*-decane. The surface of the alkali metal must be free of impurities or products of the reaction (RM and MX). Success may depend on the choice of alkyl halide, the solvent, and temperature (T), which must be below the decomposition T of the organoalkali in the solvent utilized, and the reaction must be conducted under an inert atmosphere, normally  $\text{N}_2$ .

For example, *n*-pentylsodium may be prepared<sup>2</sup> in 80–90% yield by reaction between Na sand (25  $\mu\text{m}$  particle size) and 1-chloropentane in *n*-pentane at  $-10^\circ\text{C}$  in a creased flask equipped with a high-speed stirrer<sup>3</sup>. Comparable yields of *n*-pentylsodium may be obtained in *n*-heptane, in which the yield of organoalkali decreases only from 85 to 75% after storage at RT for 24 days<sup>4</sup>. In contrast, in *n*- $\text{Bu}_2\text{O}$  the yield of *n*-pentylsodium is 63%, but after 10 days most of the reagent has decomposed by reaction with the solvent. In 1,2-dimethoxyethane (DME) and  $\text{Et}_2\text{O}$  the yields of *n*-pentylsodium are<sup>4</sup> < 15%. Even under inert solvents samples of *n*-pentylsodium must be prepared and stored at RT or lower because pyrolysis<sup>5</sup> is appreciable at  $50^\circ\text{C}$  and rapid at  $100^\circ\text{C}$ .

In contrast, triphenylchloromethane does not react in  $\text{Et}_2\text{O}$  with Na sand<sup>6</sup>. The Na surface is covered so tightly with impurities as it is prepared that the bulky triphenylchloromethane (unlike smaller 1-chloropentane) cannot penetrate. After addition of sharp particles of glass and shaking, even seed-sized (ca. 0.5 mm) particles of Na can be induced to react<sup>7,8</sup>. Alternatively, the addition of benzophenone, tetraphenylethylene, chlorobenzene, bromobenzene, or *n*-butyl chloride can bring about reaction<sup>6</sup>. These compounds may function as Na carriers (shown for benzophenone and tetraphenylethylene by formation of known Na complexes), or to clean the surface of the Na metal. For laboratory preparations of triphenylmethyllsodium, triphenylchloromethane is reacted

5.5. Formation of Bonds between Elements of Groups IVB and IA 149  
5.5.3. Carbon–Group-IA Bonds

possible at each stage owing to metal atom vacancies or to a nonuniform spacing of the metal layers.

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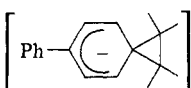
with Na amalgam in  $\text{Et}_2\text{O}$  to give an almost quantitative yield<sup>9-11</sup>. Triphenylmethylrubidium and -cesium are prepared similarly from the corresponding amalgams; however, the latter also may be prepared by reacting the chloride with finely powdered Cs metal<sup>12</sup>.

Improved mechanical stirring and procedures are used<sup>13-16</sup> to make Na dispersions of 10–15  $\mu\text{m}$ . Where the dispersion is to be used immediately no dispersing agent is necessary, but for storage or dilution 0.24–0.50 wt % of oleic acid or higher fatty alcohol is added to stabilize the dispersion. Quantitative yields of phenylsodium are obtained<sup>17</sup> by reacting chlorobenzene with these dispersions in n-pentane, benzene, n- and iso-octane, toluene, and ethylbenzene at 25–30°C. The reaction is more rapid in benzenoid hydrocarbons and does not require high-speed stirring.

Ultrasonic radiation<sup>18</sup> gives deep blue or purple Na dispersions in petroleum jelly in which the Na particles are  $\leq 1 \mu\text{m}$ , whereas good mechanical high-speed stirring at  $1-2 \times 10^4$  rpm gives gray, 3–25  $\mu\text{m}$  dispersions. The finer Na dispersion gives a faster initial rate and improved control of the reaction with chlorobenzene<sup>18,19</sup>. Fine gray-blue potassium dispersions can also be made by the ultrasonic technique in methylcyclohexane containing a trace of oleic acid; reaction with chlorobenzene at 20°C gives a suspension of phenylpotassium, in 98 % yield<sup>20</sup>, which is stable for months in an inert atmosphere at  $-10^\circ\text{C}$ .

If too much organic halide is added to Na or K dispersions a sudden rise in T may occur accompanied by an uncontrolled reaction that may result in explosion if reaction mixture is pushed out of the reaction vessel into the atmosphere<sup>18</sup>. For this reason and because of the fragility of the usual glass apparatus the customary apparatus for alkali-metal reactions should be contained within a second inert atmosphere, such as inside a glove box filled with  $\text{N}_2$ .

TABLE I. TYPICAL REACTIONS OF ORGANIC HALIDES WITH ALKALI METALS<sup>a</sup>

Example no.	Alkyl halide	Alkali metal	T (°C)	Solvent	Product	Yield (%)	Ref.
1	$(\text{CH}_3)_3\text{CCH}_2\text{Cl}$	Na	-10	n-C <sub>6</sub> H <sub>12</sub>	$(\text{CH}_3)_3\text{CCH}_2\text{Na}$	60–75	22
2	$(\text{CH}_3)_3\text{CCH}_2\text{Cl}$	K	-10	n-C <sub>6</sub> H <sub>12</sub>	$(\text{CH}_3)_3\text{CCH}_2\text{K}$	15–20 <sup>b</sup>	23
3	p-ClC <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub>	Na	10	n-C <sub>10</sub> H <sub>22</sub>	p-NaC <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub>	75 <sup>c</sup>	25
4	p-ClC <sub>6</sub> H <sub>4</sub> CCl <sub>2</sub> H <sub>5</sub>	Na	25	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CHNa(CH <sub>3</sub> )	42 <sup>d</sup>	25
5	n-C <sub>10</sub> H <sub>21</sub> CH=CHBr	K	25	n-C <sub>8</sub> H <sub>18</sub>	n-C <sub>10</sub> H <sub>21</sub> CH=CHK	32 <sup>e</sup>	24
6	Ph <sub>3</sub> CCH <sub>2</sub> Cl	Na	101	1,4-Dioxane	Ph <sub>2</sub> CNa(CH <sub>2</sub> Ph)	43	8
7	Ph <sub>3</sub> CCH <sub>2</sub> Cl	K	65	THF	Ph <sub>2</sub> CK(CH <sub>2</sub> Ph)	72 <sup>f</sup>	28
8	p-PhC <sub>6</sub> H <sub>4</sub> C(CH <sub>3</sub> ) <sub>2</sub> -C(CH <sub>3</sub> ) <sub>2</sub> Cl	Cs-K-Na	-75	THF	 Cs <sup>+</sup>	28 <sup>g</sup>	30

<sup>a</sup> The examples are chosen to be instructive rather than to illustrate the highest yields that may be obtainable. Indeed, most of these reactions can be run in higher yields by improved techniques, such as some of those mentioned in the text.

<sup>b</sup> The remaining organopotassium products (40–60%) are metallation products of 1,1-dimethylcyclopropane, 2-methyl-2-butene and 2-methyl-1-butene in a ratio of 3.8 : 1.5 : 1 as judged by the products of protonation.

<sup>c</sup> The reaction time is 1 h; no other organosodium product is detected.

<sup>d</sup> The reaction with Na metal is initially at 10°C for 1 h and then at RT for 20 h; other products are 3 % each of meta and para isomers of NaC<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H<sub>5</sub>.

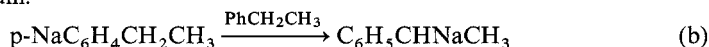
<sup>e</sup> In addition, on carbonation, 7% yield of tridecanoic acid and 8% of 2-tridecynoic acid are obtained.

<sup>f</sup> In addition 5% of Ph<sub>2</sub>CHK is produced.

<sup>g</sup> In addition 7% of PhC<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>Cs is produced (see text).

Other reactions<sup>21</sup> are given in Table 1. Neopentyl chloride (example 1, Table 1) reacts with Na sand to give neopentylsodium in good yields, as expected by analogy with n-pentyl chloride. However, the corresponding reaction of neopentyl chloride with potassium sand (example 2) gives a poor yield of neopentylpotassium; the neopentylpotassium reacts more readily with neopentyl chloride than does neopentylsodium, so products occur from  $\alpha$ , elimination with rearrangement to 1,1-dimethylcyclopropane and 2-methyl-2-butene, which in turn are metallated by neopentylpotassium. Attempts to improve the yield of neopentylpotassium by cooling to  $-50^{\circ}\text{C}$  lead to the same result<sup>22</sup>. Similar difficulties are encountered in attempts to prepare n-propyl-, n-butyl- and n-ampylpotassium by the same technique<sup>23</sup>. Ultrasonic techniques<sup>18,20</sup> may lead to improved results.

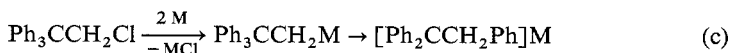
p-Chloroethylbenzene (example 3) with Na in decane at  $10^{\circ}\text{C}$  gives the expected product; however, in ethylbenzene (example 4) at RT for 30 h, the more thermodynamically stable  $\alpha$ -metallation product forms by metallation of the solvent by the initial p-ethylphenylsodium:



Similarly, p-chlorocumene reacts at  $25^{\circ}\text{C}$  with potassium in cumene to give, after 4 h, a product distribution of 60%  $\alpha$ -, 23% m- and 17% p-cumylpotassium; after 20 h the product is entirely  $\alpha$ -cumylpotassium<sup>26</sup>.

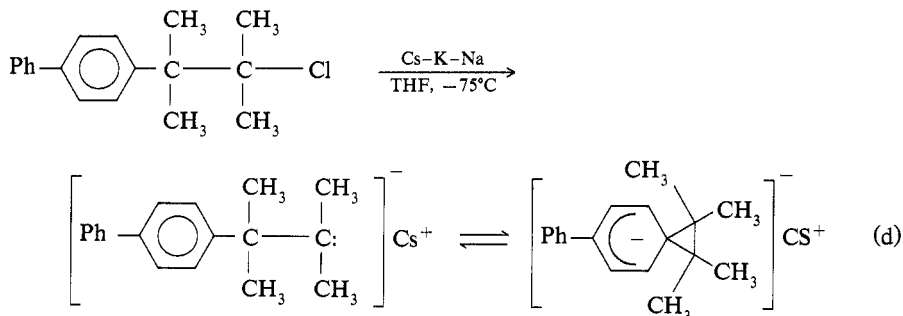
1-Bromo-1-dodecene reacts with potassium (example 5) to give, after 15 min, chiefly the expected product (see Table 1); however, after 29 h, 62.5% of the product is now the thermodynamically more stable allylic metallation product,  $[\text{n-C}_9\text{H}_{19}\text{CH}=\text{CH}=\text{CH}_2]\text{K}$ . In contrast to potassium, with Na only 7% of the product is the corresponding allylic Na compound after 24 h. Potassium compounds rearrange more readily than Na compounds<sup>24</sup>.

The final examples in Table 1 involve use of liquid alkali metals or alloys in ethers. 2-Chloro-1,1,1-triphenylethane does not react with Na sand in pentane<sup>8</sup> or in higher bp petroleum solvents<sup>27</sup> (cf. the earlier discussion of triphenylchloromethane); however, this halide reacts with molten Na in refluxing 1,4-dioxane (example 6) or with molten potassium in refluxing THF (example 7). If well-stirred, liquid metals present a clean surface for reaction. After  $\text{Et}_2\text{O}$  is added to an isooctane suspension of Na sand, however, reaction with 2-chloro-1,1,1-triphenylethane occurs<sup>29</sup> when stirring is efficient<sup>3</sup>. In hydrocarbons the products coat the surface of the Na sand and inhibit reaction. 1,1,2-Triphenylethylsodium, however, being soluble in ethers, is washed from the surface of the Na, and during this process the attachment of NaCl is weakened. Nevertheless, although n-pentylsodium is insoluble in n-pentane, it does not form a coating on Na sand tight enough to block access of n-pentyl chloride. Whether a particular organic halide will react with a given alkali metal in a certain solvent can be determined only by experimentation. Ethers frequently dissolve organoalkalis, but may react to give products of  $\alpha$ , and  $\beta$ , elimination. Examples 6 and 7 are successful in ethers because the expected initial products, 2,2,2-triphenylethylsodium and -potassium, rearrange readily to more stable delocalized organoalkali compounds:



and so escape reaction with the ether. The yield of organoalkali product is higher in THF than in dioxane because of the lower reactivity of THF than of dioxane toward carbanions at the prevailing T.

Example 8 illustrates the use of eutectic Cs–K–Na alloy<sup>31</sup>, mp  $-79^{\circ}\text{C}$ . This liquid alloy gives bright-blue solutions in THF owing to the solubility of Cs, especially at low T (potassium, by contrast, is only slightly soluble in THF). This metal–solvent system constitutes a powerful reducing medium that, with high-speed stirring<sup>3</sup>, reduces the organic chloride in example 8 in under 50 s to produce an equilibrium mixture of open- and spiro-organocesium compounds that have half-lives of only ca. 20 min:



When xs Cs–K–Na alloy is used, Cs reacts preferentially<sup>33</sup>.

The chief contaminants of organoalkalis made from organic halides with alkali metals [Eq. (a)] are the alkali-metal halide and unreacted alkali metal. For such organoalkalis as n-pentylsodium, which is insoluble in all solvents with which it does not react, there is no known method of purification of the product made by Eq. (a).

(E. GROVENSTEIN, JR.)

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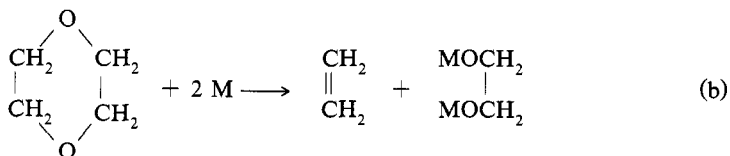
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#### 5.5.3.2.2. with Ethers.

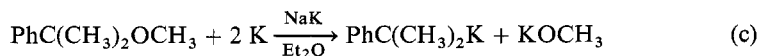
Ethers react with alkali metals:



to yield organoalkali compounds, provided that cleavage of the ether is facile below the decomposition T of the organoalkali. Simple ethers lacking unsaturation are not adequately reactive for cleavage by reaction (a). Other ethers are cleaved by alkali metals but do not give isolable organoalkali compounds; e.g., dioxane is cleaved slowly by Na–K alloy<sup>1</sup> and readily<sup>2</sup> by Cs:



Excess eutectic Na–K alloy (mp –12°C) cleaves 2-methoxy-2-phenylpropane in Et<sub>2</sub>O to give phenylisopropylpotassium in 90–96% yield<sup>3</sup>:



Here where different alkyl groups are attached to the oxygen, cleavage occurs to give the red, resonance-stabilized (or delocalized) phenylisopropylpotassium rather than the less stable methylpotassium. Also, Na–K alloy gives organopotassium, not Na compounds<sup>4</sup>. Sodium is not sufficiently active to cleave the ether at a T low enough for survival of phenylisopropylsodium which decomposes<sup>5</sup> at a little above the mp of Na. Whereas cleavage (c) gives a solution of phenylisopropylpotassium, this ether can be cleaved with

## 5.5. Formation of Bonds between Elements of Groups IVB and IA 153

## 5.5.3. Carbon-Group-IA Bonds

## 5.5.3.2. from the Group-IA Metals and Their Alloys

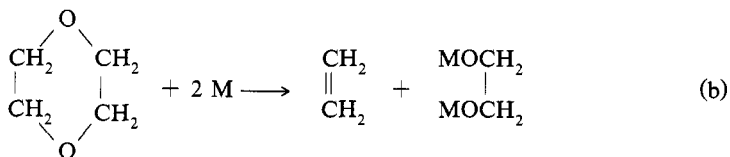
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## 5.5.3.2.2. with Ethers.

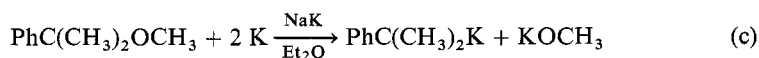
Ethers react with alkali metals:



to yield organoalkali compounds, provided that cleavage of the ether is facile below the decomposition T of the organoalkali. Simple ethers lacking unsaturation are not adequately reactive for cleavage by reaction (a). Other ethers are cleaved by alkali metals but do not give isolable organoalkali compounds; e.g., dioxane is cleaved slowly by Na–K alloy<sup>1</sup> and readily<sup>2</sup> by Cs:



Excess eutectic Na–K alloy (mp –12°C) cleaves 2-methoxy-2-phenylpropane in Et<sub>2</sub>O to give phenylisopropylpotassium in 90–96% yield<sup>3</sup>:

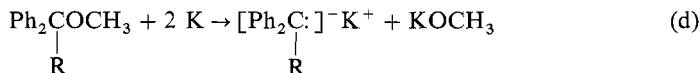


Here where different alkyl groups are attached to the oxygen, cleavage occurs to give the red, resonance-stabilized (or delocalized) phenylisopropylpotassium rather than the less stable methylpotassium. Also, Na–K alloy gives organopotassium, not Na compounds<sup>4</sup>. Sodium is not sufficiently active to cleave the ether at a T low enough for survival of phenylisopropylsodium which decomposes<sup>5</sup> at a little above the mp of Na. Whereas cleavage (c) gives a solution of phenylisopropylpotassium, this ether can be cleaved with



molten potassium at ca. 70°C in heptane or isooctane to give a deep-red suspension of phenylisopropylpotassium mixed with potassium methoxide. The organopotassium separates from potassium methoxide on solution in Et<sub>2</sub>O, filtration or decantation to remove potassium methoxide, and finally reprecipitation with hexane<sup>5</sup>.

The methyl ethers of many aryl carbinols cleave<sup>6-8</sup> in Et<sub>2</sub>O with liq Na-K alloy or with potassium powder (reaction of the latter is facilitated with the aid of small-edged pieces of quartz glass to cut through incrustations on the potassium on shaking), e.g.:



Other typical preparations of organoalkali compounds by cleavage of ethers with alkali metals are listed in Table 1. In examples 1 and 2 (Table 1), diallyl ether is cleaved by both Na and potassium sand at mild T on high-speed stirring<sup>9</sup>. Even anisole (example 3) is cleaved by potassium sand to give phenylpotassium in good yield, but anisole with the 2:1 adduct of Li and biphenyl in tetrahydrofuran (THF) at 66°C gives C<sub>6</sub>H<sub>5</sub>OLi in 55-80% yield (and likely CH<sub>4</sub>)<sup>13</sup>.

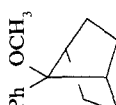
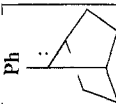
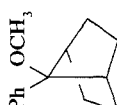
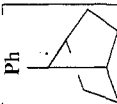
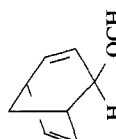
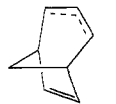
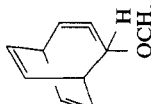

Ethers differ greatly in their rate of cleavage by alkali metals. Because the products and, likely, the transition states for ether cleavage are more ionic than the reactants, the rate of cleavage in various solvents increases<sup>14</sup>: 2-methyltetrahydrofuran ≤ tetrahydropyran < THF < 1,2-dimethoxyethane (DME) which is the order of increasing solvating power of ethers toward organoalkali compounds, with Et<sub>2</sub>O even a poorer solvent than 2-methyltetrahydrofuran<sup>15</sup>. Unfortunately, the stability of organoalkalis in ethers decreases with increase in solvating power of the solvent. Finally, the rate of cleavage of ethers by the alkali metals increases<sup>14,16</sup> Li < Na < K < Rb < Cs.

Cesium sand in THF (blue solution) cleaves 2-methoxy, 2-phenylpropane in excellent yield (example 4). The yield should not be permitted to exceed 90%, because continued reaction with Cs leads to unclear side reactions. The same ether in THF reacts with a film of potassium on the walls of the vessel to give the expected phenylisopropylpotassium; however, under these conditions of limited contact of the ether with potassium, the phenylisopropylpotassium reacts<sup>18</sup> with the starting ether to give a dimeric hydrocarbon, C<sub>18</sub>H<sub>22</sub>. Therefore, although the preparation of organoalkalis by cleavage of ethers [Eq. (a)] is not as susceptible to destruction of the products by reaction with starting materials as is the preparation of organoalkalis by cleavage of organic halides [Eq. (a) §5.5.3.2.1], such side reactions do occur and the same precautions need to be taken to prevent their occurrence as discussed in §5.5.3.2.1.

Cleavage of ethers can be the method of choice for preparations of carbanions of novel structure. The preparation of 7-phenylnorbornylpotassium and -cesium is well described (examples 5 and 6). With Na-K alloy the organoalkali product contains 97.5% K, 0.7% Na, and 1.8% Cs, whereas with Cs-K-Na alloy the composition is 99.8% Cs, 0.1% K, and 0.1% Na. The latter cleavage can be performed at lower T. Although these organoalkalis can be stored in THF for 2 months at -78°C, warming to RT for 30-60 min causes decomposition. The reaction of the organoalkalis with DME is faster than with THF and is active enough to prevent preparation in this solvent.

The cleavage of ethers by alkali metals, like cleavage of alkyl halides, does not necessarily give products of the same structure, or even the same carbon content, as the

TABLE 1. TYPICAL PREPARATION OF ORGANOALKALI COMPOUNDS BY CLEAVAGE OF ETHERS WITH ALKALI METALS

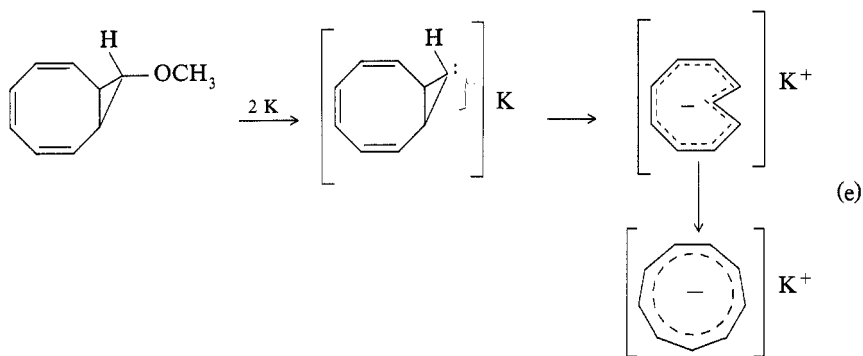
Example no.	Ether	Alkali metal	T (°C)	Solvent	Product	Yield (%)	Ref.
1	$(\text{CH}_2 = \text{CHCH}_2)_2\text{O}$	Na	35	Hexane	$[\text{CH}_2 = \text{CHCH}_2]_n\text{Na}$	77 <sup>a</sup>	10
2	$(\text{CH}_2 = \text{CHCH}_2)_2\text{O}$	K	10-30	Decane	$[\text{CH}_2 = \text{CHCH}_2]_n\text{K}$	ca 70 <sup>b</sup>	11
3	$\text{C}_6\text{H}_5\text{OCH}_3$	K	25-30	Heptane	$[\text{C}_6\text{H}_5]_n\text{K}$	60	12
4	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OCH}_3$	Cs	25	THF	$[\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2]_n\text{Cs}$	> 90	17
5		Na-K	-10 to -5	THF	 K	> 55	19
6		Cs-K-Na	-40	THF	 Cs	—	19
7		Na-K	0	THF or DME	 K	—	20,21 <sup>c</sup>
8		Na-K	-10	THF or DME	 K	ca. 80	22 <sup>c</sup>

<sup>a</sup> The yield is based on Na, the limiting reagent; other yields are based on the ether cleaved.

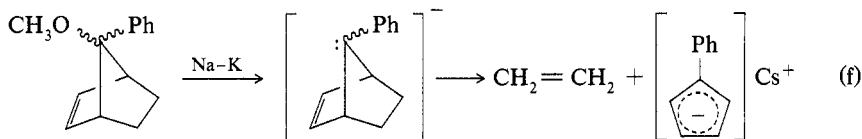
<sup>b</sup> A little isopropyl alcohol is added before the ether; in the absence of this alcohol the yield is ca 58%.

<sup>c</sup> For clarity the products are written as allylic anions; the authors favor bis-homoaromatic or bicycloaromatic structures. The structure of nonclassical carbon-ions is as controversial as that of nonclassical carbonium ions.

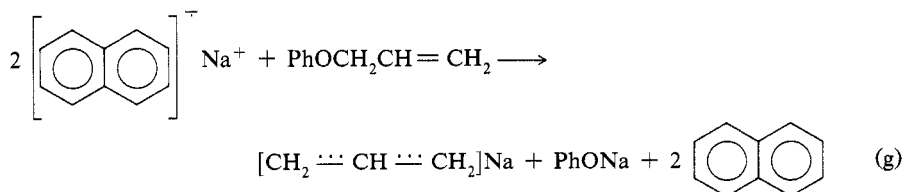
starting ether. For example, anti-9-methoxy-cis-bicyclo[6.1.0]nona-2,4,6-triene reacts with potassium in THF- $d_8$  at  $-40^\circ\text{C}$ :



with conrotatory ring opening<sup>23</sup> to give potassium trans,cis,cis,cis-cyclononatetraenide or, on warming to  $25^\circ\text{C}$ , potassium cis,cis,cis,cis-cyclononatetraenide in quantitative yield<sup>24</sup>. Also, a mixture of syn- and anti-7-phenyl-7-methoxynorbornene upon reaction with Na-K alloy in 1,2-dimethoxyethane at RT gives ethylene and potassium phenylcyclopentadienide<sup>25</sup>:



Cleavage of ethers also can be brought about by carriers of alkali metals, such as sodium naphthalenide. For example, allyl Na is preparable<sup>26</sup> in 50% yield by cleavage of allyl phenyl ether by Na naphthalenide in THF at  $-20^\circ\text{C}$ :



This reaction, however, competes with coupling to give diallyl in ca. 40% yield<sup>27</sup>. Triphenylmethylsodium can be prepared in 80% yield by cleavage of the methyl ether of triphenylcarbinol with Na naphthalenide<sup>27</sup> in THF. By comparison, allyl chloride with Na naphthalenide gives only diallyl<sup>28</sup> and benzyl chloride dibenzyl<sup>29</sup> in 86% yield. Again, coupling is a less important side reaction with ethers than with halides. The lithium radical anion of di-*t*-butylbiphenyl is superior to the corresponding naphthalene or di-*tert*-butylnaphthalene radical anion for production of alkyl lithium reagents

(93–95% yield) by reaction with alkyl halides<sup>32</sup>. Similarly, cleavage of benzyl methyl ethers,  $\text{PhCR}_2\text{OCH}_3$ , by the potassium radical anion of di-*t*-butylbiphenyl in THF at  $-78^\circ\text{C}$  is the best method of preparing the corresponding benzylpotassium compounds,  $\text{PhCR}_2\text{K}$ <sup>33</sup>.

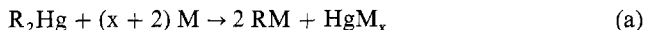
Finally, thioethers (sulfides) react more readily with alkali metals than ordinary ethers. Thioanisole is cleaved quantitatively by potassium in toluene to give potassium thiophenoxide, methane and benzylpotassium<sup>30</sup>. Cleavage of  $\text{PhC}(\text{CH}_3)_2\text{SPh}$  by potassium naphthalenide in THF– $\text{Et}_2\text{O}$  at  $-10^\circ\text{C}$  to  $-60^\circ\text{C}$  gives  $\text{PhC}(\text{CH}_3)_2\text{K}$  in 80% yield; when a potassium dispersion is used, the yield is<sup>30</sup> 88% at  $-10$  to  $-20^\circ\text{C}$ . Similarly,  $\text{Ph}_2\text{C}(\text{CH}_3)\text{SPh}$  is cleaved by an Na dispersion in THF at RT to give  $\text{Ph}_2\text{C}(\text{CH}_3)\text{Na}$  in 89% yield<sup>31</sup>.

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**5.5.3.2.3. with Organomercurials.**

Organoalkalis are prepared from organomercurials<sup>1</sup> with xs alkali metal, M:



This reaction is reversible<sup>2</sup> and, therefore, a large xs of alkali metal is used to shift the equilibrium to the right. This preparative method is general and has the advantage over the cleavage of halides and ethers (§5.5.3.2.1 and §5.5.3.2.2) that the organometallic product does not react (at the mild T of the preparation) with the starting organomercurial. Therefore, this method rarely fails<sup>2</sup>.

Typical preparations are given in Table 1. The organoalkalis produced can be freed of xs metal and other impurities<sup>1</sup> and are used in structural<sup>4,5</sup>, NMR<sup>11</sup> and UV<sup>12</sup> studies. Preparations by this procedure are run on a small scale because of the expense and toxicity of Hg compounds. The yields range from poor to excellent; low yields may result from the failure to use a large xs of alkali metal or to establish adequate contact between the metal and the organomercurial in the time allowed for reaction (see §5.5.3.2.1 for a discussion of methods of bringing about reactions of alkali metals). Another reason is because of reaction of the organoalkali compounds with solvent. For example, n-butylium and n-pentylpotassium react even with saturated hydrocarbons<sup>7</sup>. Also, these compounds undergo significant pyrolysis after standing but a few hours at RT<sup>7,13</sup>. Even benzylsodium in tetrahydrofuran (THF) at RT has a half-life of only ca. 1 day<sup>12</sup>.

The cleavage of organomercurials by alkali metals is limited by the instability and difficulty of preparation of the required Hg compounds. The Hg compound can be prepared in the example  $[(\text{CH}_3)_3\text{CCPh}_2\text{CH}_2]_2\text{Hg}$ , whereas attempts to make the corresponding alkyl chloride for cleavage fail<sup>14</sup>.

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TABLE 1. TYPICAL PREPARATIONS OF ORGANOALKALIES BY REACTION OF ORGANO MERCURIALS WITH ALKALI METALS

Example No.	Organomercurial	Alkali metal	$\frac{M}{R_2Hg}$ <sup>a</sup>	T (°C)	Time (h)	Solvent	Product	Yield (%)	Refs.
1	(CH <sub>3</sub> ) <sub>2</sub> Hg	Na <sup>b</sup>	4-10	25	3	None	CH <sub>3</sub> Na	ca. 100	3
2	(CH <sub>3</sub> ) <sub>2</sub> Hg	K <sup>c</sup>	3.6	25	—	None	CH <sub>3</sub> K	ca. 100 <sup>d</sup>	3
3	(CH <sub>3</sub> ) <sub>2</sub> Hg	Na-K	—	25	—	—	CH <sub>3</sub> K	—	4
4	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> Hg	Na <sup>b</sup>	13	25	12	None	CH <sub>3</sub> CH <sub>2</sub> Na	ca. 94	5
5	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> Hg	Na <sup>c</sup>	—	25	24-48	n-Hexane	CH <sub>3</sub> CH <sub>2</sub> Na	—	6
6	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Hg	K <sup>f</sup>	2.2	10-35	4	n-Pentane	(n-C <sub>4</sub> H <sub>9</sub> )K <sup>g</sup>	28	7
7	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Hg	K <sup>f</sup>	2.2	10-35	4	n-Hexane	(n-C <sub>4</sub> H <sub>9</sub> )K <sup>g</sup>	59	7
8	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Hg	K <sup>f</sup>	4	-60	1-2	THF-heptane <sup>h</sup>	n-C <sub>4</sub> H <sub>9</sub> K	51 <sup>i</sup>	8,9
9	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Hg	Cs <sup>f</sup>	4	-60	0.25	THF-heptane <sup>h</sup>	n-C <sub>4</sub> H <sub>9</sub> Cs	33 <sup>i</sup>	8,9
10	(n-C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> Hg	Na <sup>f</sup>	3	25	3	Pentane	n-C <sub>5</sub> H <sub>11</sub> Na	47 <sup>j</sup>	10
11	(n-C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> Hg	K <sup>f</sup>	2.2	10-35	4	Cyclohexane	(n-C <sub>5</sub> H <sub>11</sub> )K <sup>g</sup>	30	7
12	(CH <sub>2</sub> ≡CHCH <sub>2</sub> ) <sub>2</sub> Hg	M <sup>k</sup>	—	-20	0.5	THF	CH <sub>2</sub> ≡CHCH <sub>2</sub> M	—	11
13	(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> Hg	Na <sup>b</sup>	—	—	—	THF	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Na	76	12

<sup>a</sup> Ratio of alkali metal (g-at) to R<sub>2</sub>Hg (moles).

<sup>b</sup> Sodium mirror.

<sup>c</sup> Potassium mirror.

<sup>d</sup> However, repeat runs contain unreacted (CH<sub>3</sub>)<sub>2</sub>Hg.

<sup>e</sup> Sodium ribbon.

<sup>f</sup> Finely divided metal or sand.

<sup>g</sup> Impure product; see text.

<sup>h</sup> Tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) with an equal volume of heptane.

<sup>i</sup> The yield cited is that of the carboxylic acid from metalation of thiophene or 3-methylthiophene.

<sup>j</sup> Average yield of six runs.

<sup>k</sup> M = Na, K, Rb or Cs as a film inside reaction flask.

**5.5.3.2.4. with Adducts of Conjugated Hydrocarbons in Donor Solvents.**

The preparation of adducts of conjugated hydrocarbons, especially aromatic hydrocarbons, by reaction with alkali metals, M:

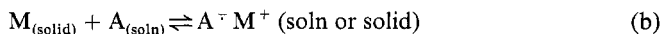


has its origin in the discovery that potassium when fused with naphthalene gives a black addition product<sup>1-5</sup>, and that donor solvents, such as Me<sub>2</sub>O or 1,2-dimethoxyethane (DME), stabilize the adducts<sup>6,7</sup>. Electron spin resonance (ESR)<sup>8,9</sup> (and magnetic susceptibility<sup>10</sup>) establish the paramagnetic properties of many alkali-metal adducts (anion radicals) and the delocalization of the electron supplied by the alkali metal. The behavior of ionic alkali-metal addition products in donor solvents—including solvation, ionization, ion pairing, and higher ionic aggregation—is complex<sup>11,12</sup>.

The preparation of adducts of conjugated hydrocarbons by reaction with alkali metals demands absence of O<sub>2</sub>, H<sub>2</sub>O or solvent impurities that can combine with the organometallic product or the alkali metal. The T must be below the decomposition point of the organoalkali compound in the particular solvent. Adequate contact between the alkali metal and the hydrocarbon must be established. In small-scale preparations the alkali metal is deposited as a mirror on the walls of the reaction vessel, where it can come in contact with solvent. In larger scale or synthetic preparations the alkali metal is in the form of a sand or dispersion (see §5.5.3.2.1), and good stirring may be helpful.

No difficulty is experienced in effecting reaction between alkali metals and conjugated hydrocarbons provided that reaction (a) is run such that the equilibrium favors the products rather than the reactants, and provided that the products are stable under these conditions. Selecting these conditions is the chief experimental problem. In reactions of benzene, biphenyl, naphthalene, and anthracene with alkali metals, theory and practice<sup>13-18</sup> agree that the electron affinities are: benzene < biphenyl < naphthalene < anthracene. What conditions are most favorable for each hydrocarbon?

Reaction (a) between alkali metal, M, and hydrocarbon, A, may be rewritten in the more complete form:

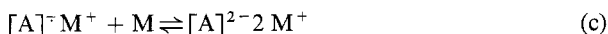


The heat of sublimation of alkali metals and the ionization potential of their atoms decrease Li > Na > K > Rb > Cs. If these were the only factors, the reducing power of the alkali metals would increase from Li to Cs. However, the effect of the solvent in Eq. (b) must be considered. Because the heat of solution of hydrocarbons in organic solvents is small, solvent mainly affects the reduction product. The dissociation of ion pairs into free ions in most organic solvents is negligible (because of strong electrostatic attraction between ions of opposite charge), so it is the solvation of ion pairs which is important. In poorly solvating media the order of reducing power should increase from Li to Cs, but in powerfully solvating donor solvents the order of reducing power is reversed because the smaller the alkali-metal cation the stronger is its solvation. If the alkali-metal adduct is a solid, its lattice energy is important and also whether it contains solvent of crystallization.

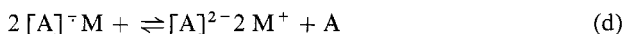
The solvating ability<sup>19</sup> of ethers for alkali-metal cations increases Et<sub>2</sub>O ≤ 1,4-dioxane < 2-methyltetrahydrofuran (MeTHF) ≤ tetrahydropyran (THP) < tetrahydrofuran (THF) < DME (glyme) < CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub> (diglyme) < CH<sub>3</sub>O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub> (triglyme = Tg) < CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>3</sub> (tetraglyme = Ttg). This series may be rationalized on the basis of steric effects, e.g., THF < Et<sub>2</sub>O and THF <

MeTHF, and a chelating effect, e.g., glyme > THF and diglyme > glyme. Furthermore, there are differing extents<sup>11-12</sup> of solvation of ion pairs: loose ion pairs have the cation separated from the anion by an intervening solvent shell chiefly about the cation; tight ion pairs lack such solvent separation, and, therefore, are contact or intimate ion pairs. However, even tight ion pairs may be solvated as externally solvated ion pairs. Cooling the solvent increases the extent of solvation; therefore, because radical-anion formation has negligible activation energy, adducts of hydrocarbons are made from RT to the freezing point of the donor solvent.

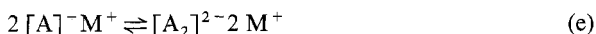
Finally, radical-anion adducts of hydrocarbons may be reduced by further reaction with alkali metal to produce dianions that are diamagnetic:



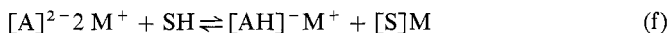
Alternatively, these dianions may be formed by disproportionation of anion radicals:



Some anion radicals couple to form dimer dianions:

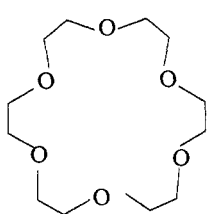


Moreover, anion radicals—or especially dianions—may undergo protonation by the solvent or other proton donor (SH):

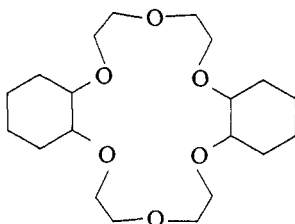


Optimum conditions for preparing alkali-metal adducts are, therefore, hard to predict; critical variables are solvent, T, time, alkali metal, and the structure of the conjugated hydrocarbon.

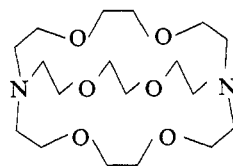
Benzene is most difficult to convert to an anion radical; nevertheless, with potassium at  $-80^\circ\text{C}$  in DME the anion radical of benzene can be identified<sup>13,20</sup> by ESR. Spin-concentration measurements on benzene in 2:1 by volume of THF:DME with Na-K alloy at  $-83^\circ\text{C}$  show that at equilibrium only ca. 0.1% benzene is converted<sup>21</sup> to radical anion. Benzene also forms an anion radical<sup>22</sup> by ESR with Rb and Cs in THF and DME, but not with Na or Li in THF-DME. Alkyl substitution destabilizes the radical anions as prepared with Na-K in THF-DME at  $-100^\circ\text{C}$ , with destabilization increasing with size [ $\text{CH}_3 < \text{CH}_2\text{CH}_3 < \text{CH}(\text{CH}_3)_2 < \text{C}(\text{CH}_3)_3$ ] and with numbers of such groups<sup>23</sup>. In contrast,  $\text{Si}(\text{CH}_3)_3$ ,  $\text{Ge}(\text{CH}_3)_3$ , CN and  $\text{NO}_2$  groups stabilize their benzene radical anions<sup>24</sup>. Radical-anion formation even in benzene, toluene, or mesitylene with potassium can be brought about by addition of dicyclohexyl-18-crown-6<sup>25,26</sup>, 18-crown-6<sup>27</sup> or [2.2.2]cryptate<sup>25</sup> at RT or lower. Radical anions may be prepared similarly<sup>25,27</sup> from Rb and Cs, but not from Na with 18-crown-6 or [2.2.2]cryptand<sup>27</sup>. The yield or how long such solutions are stable is not known.



18-Crown-6



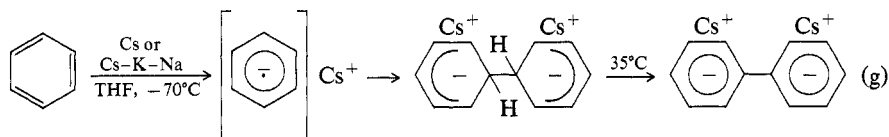
Dicyclohexyl-18-crown-6



[2.2.2]Cryptand



Cesium sand reacts with xs benzene in THF at  $-70^{\circ}\text{C}$  with conversion of ca. 80% of the Cs into Cs benzenide, which is formed as a black precipitate<sup>28</sup>. Slowly at  $-70^{\circ}\text{C}$ , or more readily when warmed to  $5^{\circ}\text{C}$ , the Cs benzenide gives the yellow, solid dimer dianion, which when warmed to  $35^{\circ}\text{C}$  gives dicesium biphenylide as a black solid:



Similar reactions occur with Cs-K-Na alloy, Cs being the metal that is extracted preponderantly from the alloy by benzene (or toluene)<sup>28</sup>.

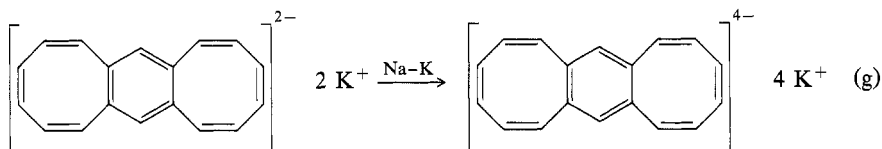
Unlike benzene, biphenyl reacts with Na in THF at  $25^{\circ}\text{C}$ ; however, reaction (a) is reversible<sup>10</sup> and goes only to ca. 30%. Addition of  $\text{Et}_2\text{O}$  to the THF displaces the equilibrium to the left with precipitation of finely divided Na. Also, although a crystalline product separates from a concentrated solution of sodium biphenylide ( $\text{NaBp}$ ) at  $-78^{\circ}\text{C}$ , attempts to remove all of the THF from these crystals result in decomposition<sup>29</sup> with cleavage of Na. As the solvating power of the medium increases, biphenyl reacts more completely with Na; in DME the conversion to  $\text{NaBp}$  is quantitative. With triglyme ( $\text{Tg}$ ), blue crystals of the solvent-separated ion pairs<sup>30</sup>,  $\text{NaBp} \cdot 2 \text{ Tg}$ , can be isolated. Similar crystals of  $\text{KBp} \cdot 2 \text{ Tg}$  and  $\text{RbBp} \cdot 2 \text{ Tg}$  are also isolable<sup>30</sup>. Potassium first reacts with biphenyl in DME to give a blue solution of paramagnetic  $\text{K}_2\text{Bp}$  [Eq. (a)]; however, continued reaction with potassium gives red-brown, diamagnetic  $\text{KBp}$  [Eq. (c)]<sup>31</sup>. This dianion is a powerful base and after 4 h 90% is consumed by reaction with the DME solvent [Eq. (f)]. Similar reactions occur between biphenyl and both Li and potassium in THF<sup>29</sup>.

Naphthalene behaves like biphenyl. With Na in  $\text{Et}_2\text{O}$  only a minute amount (ca.  $10^{-3}\%$  at  $20^{\circ}\text{C}$ ) of Na naphthalenide is produced<sup>32</sup>, however, in THF or DME the yield of the green 1:1 adduct of Na naphthalenide is quantitative<sup>6,33</sup>. Sodium naphthalenide retains its integrity and stability only as long as the solvent vapor pressure exceeds a certain saturation pressure. Removal of solvent at RT initially gives a green solid; continued removal of solvent (in vacuo) leads to desolvation and spontaneous decomposition<sup>6,34</sup> into naphthalene and Na metal. Naphthalene does not form a dianion with xs Na in THF; however, a purple dianion is formed<sup>35</sup> with xs Li provided the naphthalene concentration is low<sup>33</sup>. Potassium with naphthalene in  $\text{Et}_2\text{O}$  at  $20^{\circ}\text{C}$  gives a 13% conversion to potassium naphthalenide at equilibrium<sup>32</sup>; in THF a green potassium naphthalenide is formed initially, but continued reaction with potassium (contrary to earlier reports<sup>36</sup>) gives red-brown dipotassium naphthalenide [Eq. (c)], which, in contrast to the Li dianion<sup>37</sup>, is stable in THF.

Anthracene reacts with Na powder in  $\text{Et}_2\text{O}$  to give first the blue Na anthracenide (mononegative ion) and then, on further reaction with Na metal, a violet dinegative ion [Eq. (c)]. Disodium anthracenide is only slightly soluble in  $\text{Et}_2\text{O}$  and separates as a deep-blue powder containing no ether<sup>2</sup>. Both blue monosodium and disodium anthracenide also may be prepared<sup>39</sup> in THF. For preparation of the monosodium derivative in THF, a small deficiency of Na metal is used; the xs anthracene and THF may then be removed under high vacuum to give crystals free of THF and containing only bound Na (no  $\text{H}_2$  on hydrolysis)<sup>40</sup>. Disodium anthracenide is more stable in THF than dilithium

anthracenide, which reacts with the solvent by nucleophilic displacement on the  $\alpha$  carbon<sup>33</sup>. Both mono- and dipotassium anthracenide may also be prepared in THF<sup>41</sup>. The stability of mono- and disodium anthracenides does not depend on stabilization by donor solvents; crystal lattice forces alone are adequate<sup>40</sup>. Dilithium naphthalenide is stabilized by coordination with tetramethylethylenediamine (TMED)<sup>38</sup> in hexane and crystallizes as  $[\text{C}_{10}\text{H}_8]^{2-}[\text{Li}\cdot\text{TMED}]_2^+$ . Dilithium anthracenide likewise crystallizes from benzene-hexane<sup>42</sup> as  $[\text{C}_{14}\text{H}_{10}]^{2-}[\text{Li}\cdot\text{TMED}]_2^+$ .

Finally, tri- and even tetraanions may be prepared in suitable cases<sup>43</sup>. For example, dicyclocotatetraeno[1,2:4,5]benzene with Na-K in THF gives<sup>44</sup> first a dark emerald-green solution of a dianion, which on further reaction with Na-K gives a stable, red, insoluble tetraanion:



Both pyrene and perylene with Na in THF (or DME) also are claimed to give tetraanions<sup>45</sup>, but reinvestigation<sup>46</sup> suggests that the proposed pyrene tetraanion is 1-hydropyrenyl monoanion from protonation of the dianion [see Eq. (f)].

(E GROVENSTEIN, JR.)

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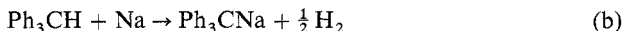
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#### 5.5.3.2.5. with Acidic Hydrocarbons Evolving H<sub>2</sub>.

Hydrocarbons react with alkali metals, evolving H<sub>2</sub>:



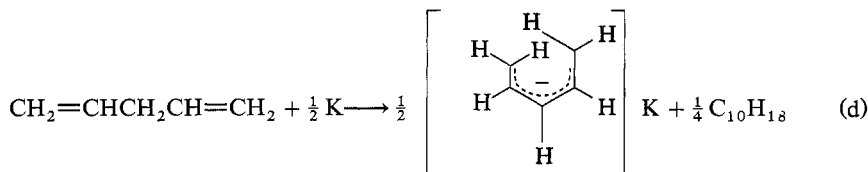
This is the simplest and most direct method of preparing organoalkalis from hydrocarbons; e.g., triphenylmethane<sup>1</sup> reacts with Na in liq NH<sub>3</sub>:



The corresponding reaction of potassium in liq NH<sub>3</sub> gives H<sub>2</sub> and triphenylmethylpotassium in 85–94% yield as judged by the yield of 1,1,1-triphenylethane<sup>2</sup> with CH<sub>3</sub>I. Hydrogen, however, although displaced from its original site by alkali metal, commonly is not evolved. For example, acetylene reacts with Na in liq NH<sub>3</sub> in good yield<sup>3</sup>:



Also 1,4-pentadiene reacts with potassium in 96% yield in the presence of equimolar triethylamine in tetrahydrofuran (THF) at 0°C:



where C<sub>10</sub>H<sub>18</sub> is a mixture of decadienes from reductive coupling of the pentadiene. Reaction (d) is also given by Na, Rb and Cs in comparable yield; similar reactions occur with both cis- and trans-1,3-pentadiene and other dienes<sup>4–6</sup>.

## 5.5. Formation of Bonds between Elements of Groups IVB and IA

### 5.5.3. Carbon-Group-IA Bonds

#### 5.5.3.2. from the Group-IA Metals and Their Alloys

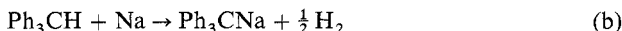
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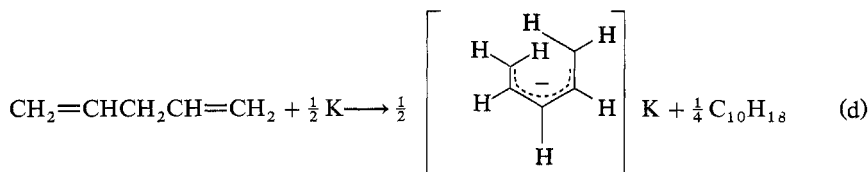
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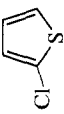
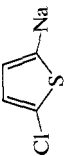
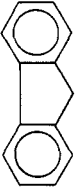



Also 1,4-pentadiene reacts with potassium in 96% yield in the presence of equimolar triethylamine in tetrahydrofuran (THF) at 0°C:



where C<sub>10</sub>H<sub>18</sub> is a mixture of decadienes from reductive coupling of the pentadiene. Reaction (d) is also given by Na, Rb and Cs in comparable yield; similar reactions occur with both cis- and trans-1,3-pentadiene and other dienes<sup>4–6</sup>.

TABLE 1. TYPICAL PREPARATIONS OF ORGANOALKALIS FROM ACIDIC HYDROCARBONS WITH ALKALI METALS

Example no.	Hydrocarbon	Alkali metal	T (°C)	Solvent	Organoalkali product	Yield (%)	Refs.
1		Na	0	THF		67-90	7
2		Na-Hg	35	Et <sub>2</sub> O		92	8
3	Ph <sub>3</sub> CH	K	138	Xylene	Ph <sub>3</sub> CK	69	9
4	Ph <sub>3</sub> CH	K	25	DME	Ph <sub>3</sub> CK	78 <sup>a</sup> , 91 <sup>b</sup>	10
5		K	22	DME		90-95	11
6	Toluene	K + Na <sub>2</sub> O	90	Toluene	PhCH <sub>2</sub> K	83-90	16
7	Toluene	Cs	20	THF	PhCH <sub>2</sub> Cs	70-88	17-19
8	Ph <sub>2</sub> CH <sub>2</sub>	K	15-40	THF	Ph <sub>2</sub> CHK	50	20
9	CH <sub>2</sub> =CHCH <sub>3</sub>	K	150	RH <sup>c</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> K <sup>d</sup>	62	21

<sup>a</sup> After protonation phenylcyclohexane (2%), phenylcyclohexadienes (2%), biphenyl (6%) and diphenylmethane (16%) are found besides triphenylmethane.

<sup>b</sup> Reaction run in presence of 2 mol equiv butadiene; trans-2-butene, octadienes and dodecatrienes are in the final product, but no diphenylmethane or phenylcyclohexane.

<sup>c</sup> Mineral oil.

<sup>d</sup> Or other compounds that give propylene on alcoholysis.

Other typical reactions of acidic hydrocarbons with alkali metals are given in Table 1. Example 4 (Table 1) shows that, in addition to hydrogenation of multiple bonds, reductive cleavage may be a complicating side reaction. In the reaction of triphenylmethane this side reaction may be eliminated by addition of butadiene which, as its radical anion, acts as proton acceptor.

The reaction of fluorene with alkali metals (example 5) proceeds by way of radical anions<sup>12,13</sup> or dianions<sup>14,15</sup> whose rate of decay increases:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ . Also, the rate depends on the solvent and increases<sup>11</sup> dioxane < THF < 1,2-dimethoxyethane (DME) as the solvating power for ions increases.

In example 6, Na<sub>2</sub>O serves as a hydrogen acceptor:



In contrast, reaction with Cs (example 7) proceeds with evolution of nearly the theoretical amount of H<sub>2</sub> [Eq. (a)].

Even a hydrocarbon as weakly acidic as propylene reacts with potassium (example 9); however, the conditions are severe and the yield of allylpotassium moderate. Catalysts induce Li to react with propylene in THF at 0°C to give either (E)-propenyllithium or allyllithium, depending on the choice of catalyst<sup>22</sup>.

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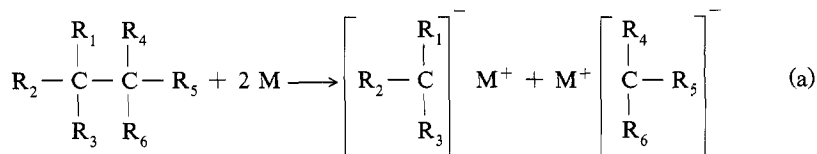
## 5.5. Formation of Bonds between Elements of Groups IVB and IA 167

## 5.5.3. Carbon-Group-IA Bonds

## 5.5.3.2. from the Group-IA Metals and Their Alloys

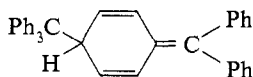
**5.5.3.2.6. by Cleavage of Carbon-Carbon Bonds.**

Hydrocarbons undergo cleavage of C—C bonds with alkali metals:



provided that the substituent groups contain adequate unsaturation<sup>1-3</sup> as illustrated in Table 1.

The compound, described in the early literature as hexaphenylethane but now known to be:



is cleaved by 1% Na-Hg in Et<sub>2</sub>O-benzene to triphenylmethylsodium<sup>3,4</sup>. This cleavage may depend on prior dissociation into the stable triphenylmethyl radical; however, with powdered Na, the hydrocarbon is isomerized<sup>1</sup> to p-benzhydryltetraphenylmethane, p-[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH]C<sub>6</sub>H<sub>4</sub>C(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

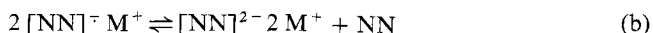
Other hydrocarbons require a more powerful reducing agent for cleavage of carbon-carbon bonds. Reducing power<sup>3-5</sup> increases 1% Na-Hg < 40% Na-Hg < Na-K < Cs-K-Na. For example, pentaphenylethane is cleaved<sup>4</sup> by Na-K, only slightly by 40% Na-Hg and not all by 1% Na-Hg. Because 1% Na-Hg reacts with triphenylmethyl radical, the failure to cleave pentaphenylethane is evidence that the cleavage which occurs with the more concentrated amalgam (or with Na-K) is a direct reductive cleavage of the C—C bond, not one involving prior dissociation into free radicals<sup>4</sup>. The other cleavages given in Table 1 are also direct reductive cleavages of C—C bonds<sup>2,7</sup>.

These cleavages occur via intermediate anion radicals or dianions. Hence, the conditions that favor formation of such intermediates favor cleavage of C—C bonds (see §5.5.3.2.4). Cleavage of monohomocyclooctatetraene (Table 1, example 15) proceeds by way of the monohomocyclooctatetraene radical anion:



characterized by ESR; further reaction with potassium metal leads to the monohomocyclooctatetraene dianion as shown in the table<sup>17,18</sup>.

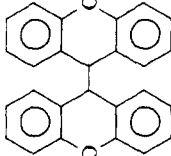
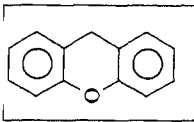
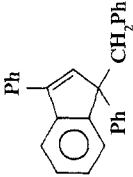
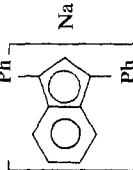

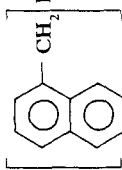
Reductive cleavage of 1,2-di(α-naphthyl)ethane (NN) proceeds via radical anions ([NN]<sup>•-</sup> M<sup>+</sup>); however, kinetic studies<sup>15</sup> show that the radical anions disproportionate to dianions:



The dianion then undergoes cleavage:



TABLE 1. TYPICAL PREPARATIONS OF ORGANOALKALIES BY CLEAVAGE OF CARBON-CARBON BONDS BY ALKALI METALS

Example No.	Hydrocarbon	Alkali metal	T (°C)	Solvent <sup>a</sup>	Product	Yield (%)	Refs.
1	$\text{Ph}_3\text{CCHPh}_2$	K	25	$\text{Et}_2\text{O}$	$\text{Ph}_3\text{CK} + \text{Ph}_2\text{CHK}$	— <sup>b</sup>	1,4
2	$\text{Ph}_2\text{CHCHPh}_2$	Na-K	25	$\text{Et}_2\text{O}$	$\text{Ph}_2\text{CHK}$	— <sup>bc</sup>	2-4
3	$\text{Ph}_3\text{CCH}_2\text{Ph}$	Na-K	25	$\text{Et}_2\text{O}$	$\text{Ph}_3\text{CK} + \text{PhCH}_2\text{K}^c$	— <sup>bd</sup>	2,4
4	$\text{Ph}_3\text{CCH}(\text{C}_6\text{H}_4\text{-p})_2$	40% Na-Hg	25	$\text{Et}_2\text{O}-\text{C}_6\text{H}_6$	$\text{Ph}_3\text{CNa} + \text{NaCH}(\text{C}_6\text{H}_4-\text{Ph-p})_2$	— <sup>b</sup>	7
5		Na-K	25	$\text{Et}_2\text{O}$		> 57% <sup>f</sup>	8
6		40% Na-Hg	25	$\text{Et}_2\text{O}$		90	9
7	$\text{Ph}_2\text{CHCH}_2\text{CH}=\text{CPh}_2$	Na-K	25	$\text{Et}_2\text{O}$	$[\text{Ph}_2\text{CH}]_2\text{K} + [\text{Ph}_2\text{C}=\text{CHCH}_2]\text{K}$	— <sup>g</sup>	10
8	$\text{p-PhC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Ph-p}$	Na-K	25	1,4-Dioxane	$[\text{p-PhC}_6\text{H}_4\text{CH}_2]\text{K}$	— <sup>g</sup>	11
9	$[(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}]_3\text{C}\equiv\text{CC}(\text{CH}_3)_3$	Na-K	25	$\text{Et}_2\text{O}$	$[(\text{CH}_3)_3\text{CC}\equiv\text{C}]\text{K}$	70-90	12
10		Na or K	25	THF		— <sup>b</sup>	13-15
11	$\text{PhCH}_2\text{CH}_2\text{Ph}$	Na-K	0	Glyme-triglyme	$[\text{PhCH}_2]\text{K}$	42	16
12	$\text{PhCH}_2\text{CH}_2\text{Ph}$	Cs-K-Na	-78	THF	$[\text{PhCH}(\text{CH}_2\text{Ph})]\text{K}$	21	5
13	meso- $\text{PhCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{Ph}$	Cs-K-Na	-78	THF	$[\text{PhCH}_2]\text{Cs}$	94	5
14	$\text{PhCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	Cs-K-Na	-78	THF	$[\text{PhCH}(\text{CH}_3)]\text{Cs}$ $[\text{PhCH}_2]\text{Cs}$ $[\text{CH}_2=\text{CHCH}_2]\text{Cs}$	100 96 91	5 5 5



15		K	-78 DME		90	17-18
16		K	-33 NH <sub>3</sub>		— <sup>b</sup>	19
17		Na-K	25 THF or DME		78 <sup>h</sup>	20
18		Na	-28 NH <sub>3</sub>		86 <sup>i</sup>	21-22
19		K	-78 MeTHF		< 90	23-25
20		K	-33 NH <sub>3</sub>		— <sup>b</sup>	26

<sup>a</sup> The solvents and abbreviations are: THF, tetrahydrofuran; DME or glyme, 1,2-dimethoxyethane; CH<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>OCH<sub>3</sub>, triglyme; MeTHF, methyltetrahydrofuran. The reaction is quantitative.

<sup>b</sup> The reaction is quantitative.

<sup>c</sup> Cleavage with dilithium biphenylide in THF gave, on carbonation diphenylacetic acid in 83% yield<sup>6</sup>.

<sup>d</sup> Cleavage with dilithium biphenylide in THF gave, on carbonation triphenylacetic acid in 93% yield and detectable phenylacetic acid<sup>6</sup>.

<sup>e</sup> Benzylpotassium (or Na) is not detected possibly because of its reaction with Et<sub>2</sub>O.

<sup>f</sup> This is the yield of recrystallized carboxylic acid from carbonation

<sup>g</sup> No yields given. <sup>h</sup> Also 15% of the monoanion from protonation of the dianion

<sup>i</sup> Also 4% of 9-isopropylfluorenylsodium.

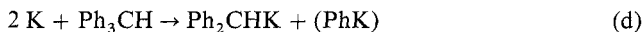
Solvents and counterions greatly influence the rate of reductive cleavage. The rate increases with decreasing polarity of the solvent and increasing size of the counterion; these are the conditions that favor tight ion pairs, which disproportionate to dianions to a greater degree than loose ones. In the solvent hexamethylphosphoramide (HMPA) in which virtually all ion pairs are dissociated into free ions, the anion radical  $[\text{NN}]^{\cdot -}$  is stable.

A side reaction in cleavage of some C—C bonds by alkali metals is cleavage of C—H bonds (see §5.5.3.2.5). In example 11 with Na—K in glyme-triglyme at 0°C, one third of the organoalkali product results from C—H cleavage; however, cooling to -78°C, as is possible with use of Cs—K—Na alloy in tetrahydrofuran (THF), eliminates this side reaction (example 12). Reductive cleavages of C—C bonds should be done at as low a T as possible; much of the modern work in Table 1 with K and Cs or their alloys is performed at -78°C.

For ready cleavage of C—C bonds by alkali metals, the products of cleavage must be stabilized by aryl groups (examples 1-6), double bonds (examples 7, 14-17, 20) or by triple bonds (example 9), one such group per anion being sufficient (examples 11-14). Also, three- and four-membered rings are cleaved readily (examples 15-20); indeed, in example 18, only one of the expected anionic centers is stabilized by unsaturated groups such that the nonstabilized anionic center is protonated by the liq-NH<sub>3</sub> solvent in the final product. In example 20 the intermediate dianion is monoprotonated by the liq-NH<sub>3</sub> solvent; however, in example 15 a similar dianion survives in the less acidic solvent, 1,2-dimethoxyethane (DME). In example 16 cleavage occurs at the carbon attached to the phenyl group; this is followed by a proton migration to give aromatic cyclooctatetraene dianion that is sufficiently stable to resist protonation even by liq NH<sub>3</sub>.

Example 19 illustrates that reductive ring opening of cis-3,4-diphenylbenzocyclobutene occurs in a stereospecific, conrotatory manner to yield the Z,E dianion; likewise, reductive cleavage of trans-3,4-diphenylbenzocyclobutane gives the corresponding (E,E) dianion<sup>23-25</sup>.

The above carbanions are stabilized by delocalization of charge onto an unsaturated group (allylic, propargylic or benzylic). In a less effective type of stabilization, the anionic charge is stabilized in an orbital having increased s character (e.g., sp<sup>2</sup> rather than sp<sup>3</sup> hybridization), e.g., in the cleavage of triphenylmethane<sup>27,28</sup>:



where yields of diphenylmethylpotassium are as high as 50%, but phenylpotassium is not found, because of reaction with triphenylmethane or the ether solvent. The related cleavages of 9,9-diarylfluorenes to 9-arylfluorenyl anions by potassium in DME occur in dianions produced by disproportionation of initially formed anion radicals<sup>29</sup>.

Phenylsilyl anions, Ph<sub>n</sub>, Ph<sub>n</sub>Me<sub>3-n</sub>SiM, can be made by cleavage<sup>30</sup> of the Si—Si bond of (Ph<sub>n</sub>Me<sub>3-n</sub>Si)<sub>2</sub> by alkali metals in THF according to the general procedures for the cleavage of C—C bonds.

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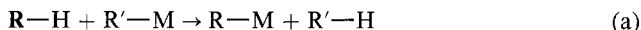
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### 5.5.3.3. from Other Group-IA Organometallics of the Same Metal

#### 5.5.3.3.1. by Proton–Metal Exchange with Acidic C—H Bonds.

Group-IA organometallics are pyrophoric and should be handled in an inert atmosphere.

Group-IA organometallics are formed from acidic hydrocarbons with more basic organometallic in acid–base or metallation reactions:



The efficiency depends upon the difference in the  $\text{pK}_\text{a}$ s of the acids<sup>1,2</sup>, which also can be a function of the solvent. The rate is a function of the base and the solvent. Such bases as MH and  $\text{MNH}_2$  are insoluble in and react slowly in hydrocarbons or ethers, but solubilization of these bases by an additive leads to rapid metallations<sup>3–5</sup>. In the polar aprotic solvents dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA) and N,N-dimethylformamide (DMF) reaction (a) is rapid. **Hexamethylphosphoramide causes tumors and should be handled in a hood with appropriate protective measures**<sup>6</sup>. Reaction

## 5.5. Formation of Bonds between Elements of Groups IVB and IA

### 5.5.3. Carbon–Group-IA Bonds

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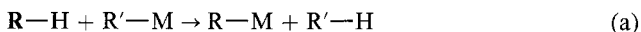
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#### 5.5.3.3. from Other Group-IA Organometallics of the Same Metal

##### 5.5.3.3.1. by Proton–Metal Exchange with Acidic C—H Bonds.

Group-IA organometallics are pyrophoric and should be handled in an inert atmosphere.

Group-IA organometallics are formed from acidic hydrocarbons with more basic organometallic in acid–base or metallation reactions:



The efficiency depends upon the difference in the  $\text{pK}_\text{a}$ s of the acids<sup>1,2</sup>, which also can be a function of the solvent. The rate is a function of the base and the solvent. Such bases as MH and  $\text{MNH}_2$  are insoluble in and react slowly in hydrocarbons or ethers, but solubilization of these bases by an additive leads to rapid metallations<sup>3–5</sup>. In the polar aprotic solvents dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA) and N,N-dimethylformamide (DMF) reaction (a) is rapid. **Hexamethylphosphoramide causes tumors and should be handled in a hood with appropriate protective measures**<sup>6</sup>. Reaction

(a) is conducted in liq  $\text{NH}_3$ , and acidic hydrocarbons ( $\text{pK}_a < 15$ ) can be metallated in alcohols or  $\text{H}_2\text{O}$ .

Active group-IA organometallics are prepared in  $\text{N}_2$  or Ar.

The strongest bases for reaction (a) are alkyl and aryl group-IA compounds prepared from metals with organic halides, ethers,  $\text{R}_2\text{Hg}$  or aromatic compounds (see §5.5.3.2) or by metal-metal exchange (see §5.5.3.3.2). Common bases are  $n\text{-C}_4\text{H}_9\text{K}$ ,  $n\text{-C}_5\text{H}_{11}\text{Na}$ ,  $\text{C}_6\text{H}_5\text{Na}$ ,  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{K}$ ,  $(\text{CH}_3)_3\text{SiCH}_2\text{K}$  and the weaker  $(\text{C}_6\text{H}_5)_3\text{CM}$  ( $\text{M} = \text{Na}, \text{K}$ ). Metallation of DMSO gives  $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{M}$  ( $\text{M} = \text{Na}, \text{K}, \text{Cs}$ ), which is used in reaction (a). The commercially available  $\text{NaH}$  and  $\text{KH}$  are useful because they are poor nucleophiles.

The group-IA amides,  $\text{NaNH}_2$  and  $\text{KNH}_2$ , are used<sup>2</sup> as bases in liq  $\text{NH}_3$ , as is  $[\text{c-C}_6\text{H}_{11}\text{NH}]\text{Cs}$  in  $\text{c-C}_6\text{H}_{11}\text{NH}_2$ . Hindered dialkylamide bases, such as  $(i\text{-Pr})_2\text{NM}$  ( $\text{M} = \text{Na}, \text{K}, \text{Cs}$ ), prepared<sup>7</sup> from  $\text{R}_2\text{NH}$  with  $\text{C}_4\text{H}_9\text{Li}$  and  $(\text{CH}_3)_3\text{COM}$ , are nonnucleophilic and soluble in ethers. The amide bases  $[(\text{CH}_3)_3\text{Si}]_2\text{NM}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) can be prepared in high purity<sup>8</sup> but are weaker.

Group-IA alkoxides metallate acidic hydrocarbons. These bases are available commercially or are prepared from the metal with an alcohol. The nonnucleophilic  $(\text{CH}_3)_3\text{COK}$  is the most widely used.

The  $\text{pK}_a$ s of the conjugate acids of commonly used bases are given in Table 1.

The most basic group-IA organometallics produced by reaction (a) are cyclopropylsodiums prepared by metallations with  $\text{C}_5\text{H}_{11}\text{Na}$ . Olefins and arenes containing no allylic or benzylic protons react with  $\text{C}_5\text{H}_{11}\text{Na}$  to give vinyl- and arylsodiums; the addition<sup>9</sup> of  $(\text{CH}_3)_3\text{COK}$  activates  $\text{C}_5\text{H}_{11}\text{Na}$ . The lack of regioselectivity limits synthetic utility.

Metallations are more useful synthetically when the substrate contains only one reactive site. The syntheses of benzyl-, allyl-, pentadienyl- and more delocalized group-IA organometallics and of group-IA acetylides are best performed by reaction (a). These preparations are not complicated by secondary coupling reactions or by contamination of the reaction mixture with other metals. Metallations of halogen-containing substrates at low T give carbenoids which are difficult to prepare by other routes.

The metallation of acidic hydrocarbons ( $\text{pK}_a$  15–30), such as ketones and esters, and their nitrogen-containing analogues are complicated because the substrates contain a reactive electrophilic center. Sterically hindered  $\text{R}_2\text{NM}$ ,  $(\text{C}_6\text{H}_5)_3\text{CM}$  or nonnucleophilic

TABLE 1. ACIDITIES OF CONJUGATE ACIDS OF COMMON BASES

Acid	Solvent	$\text{pK}_a$	Refs.
Alkanes		> 45	
$\text{C}_6\text{H}_6$	$\text{c-C}_6\text{H}_{11}\text{NH}_2$	43	2
$\text{CH}_3\text{S}(\text{O})\text{CH}_3$	DMSO	35	12
$(\text{C}_6\text{H}_5)_3\text{CH}$	Various	28–33	2
$\text{H}_2$	THF	36	4
$\text{NH}_3$		34	13
$\text{RNH}_2, \text{R}_2\text{NH}$		36–42	13,14
$(\text{CH}_3)_3\text{COH}$	$\text{H}_2\text{O}$	19 <sup>a</sup>	15
$(\text{CH}_3)_3\text{COH}$	DMSO	31	16

<sup>a</sup> The  $\text{pK}_a$ , measured in  $\text{C}_6\text{H}_6$ , is relative to the  $\text{pK}_a$  of  $\text{CH}_3\text{OH}$  in  $\text{H}_2\text{O}$ .

TABLE 2. GROUP-IA ORGANOMETALLICS FROM METALLATION REACTIONS

Reaction	Product	Refs.
Cyclopropanes + n-C <sub>5</sub> H <sub>11</sub> Na	Cyclopropylsodium <sup>a</sup>	9
Alkenes + n-C <sub>5</sub> H <sub>11</sub> Na	Vinylsodiums <sup>b</sup>	9
C <sub>6</sub> H <sub>6</sub> + n-C <sub>4</sub> H <sub>9</sub> K <sup>c</sup>	C <sub>6</sub> H <sub>5</sub> K	17
(h <sup>3</sup> -C <sub>3</sub> H <sub>3</sub> ) <sub>2</sub> Fe <sup>d</sup> + n-C <sub>5</sub> H <sub>11</sub> Na <sup>e</sup>	(h <sup>3</sup> -C <sub>5</sub> H <sub>4</sub> Na) <sub>2</sub> Fe <sup>f</sup>	18
+ n-C <sub>4</sub> H <sub>9</sub> K <sup>c</sup>	(h <sup>3</sup> -C <sub>5</sub> H <sub>4</sub> K) <sub>2</sub> Fe <sup>f</sup>	19
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> + n-C <sub>4</sub> H <sub>9</sub> K <sup>c</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> K	17
+ C <sub>6</sub> H <sub>5</sub> K <sup>e</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> K	20
+ R <sub>3</sub> NM <sup>g</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> M <sup>g</sup>	7
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub> + (CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> K	C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> K	9
p-C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> + c-C <sub>6</sub> H <sub>11</sub> NHCs	p-C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cs	14
p-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> + n-C <sub>4</sub> H <sub>9</sub> K <sup>c</sup>	p-(KCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	21
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH <sub>2</sub> + (CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> M <sup>h</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHM <sup>h</sup>	22
+ NaNH <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHNa	23
+ KH <sup>i</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHK	4
+ MH <sup>j</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHM <sup>j</sup>	5
+ C <sub>10</sub> H <sub>8</sub> Na <sup>k</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHNa	24
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH + KNH <sub>2</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CK	25
+ NaH <sup>i</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CNa	3
+ C <sub>10</sub> H <sub>8</sub> Na <sup>k</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CNa	26
CH <sub>3</sub> CH=CH <sub>2</sub> + (CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> K	CH <sub>2</sub> =CHCH <sub>2</sub> K	27
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CHO + n-C <sub>4</sub> H <sub>9</sub> K <sup>c</sup>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH=C(K)O	28
R <sub>2</sub> C=CHSeC <sub>6</sub> H <sub>5</sub> + (i-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NK	R <sub>2</sub> C=C(K)SeC <sub>6</sub> H <sub>5</sub>	29
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH=CH <sub>2</sub> + (CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> K	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> K	30
CH <sub>2</sub> =CHCH <sub>2</sub> CH=CH <sub>2</sub> + (CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> K	CH <sub>2</sub> =CHCH=CHCH <sub>2</sub> K	30
+ KNH <sub>2</sub>	CH <sub>2</sub> =CHCH=CHCH <sub>2</sub> K	31
PhCH=CHCH=CHCH <sub>2</sub> Ph + C <sub>18</sub> H <sub>20</sub> Na <sub>2</sub> <sup>m</sup>	C <sub>6</sub> H <sub>5</sub> CH=CHCH=CHCH(Na)C <sub>6</sub> H <sub>5</sub>	32
CH <sub>2</sub> =C(CH <sub>3</sub> )C(CH <sub>3</sub> )=CH <sub>2</sub> + n-BuK <sup>c</sup>	CH <sub>2</sub> =C(CH <sub>2</sub> K)C(CH <sub>2</sub> K)=CH <sub>2</sub>	33
c-C <sub>5</sub> H <sub>6</sub> + NaNH <sub>2</sub>	c-C <sub>5</sub> H <sub>5</sub> Na <sup>o</sup>	34
+ NaOC(CH <sub>3</sub> ) <sub>3</sub>	c-C <sub>5</sub> H <sub>5</sub> Na <sup>o</sup>	35
HC≡CH + NaNH <sub>2</sub>	HC≡CNa	36
C <sub>6</sub> H <sub>5</sub> C≡CH + C <sub>10</sub> H <sub>8</sub> Na <sup>k</sup>	C <sub>6</sub> H <sub>5</sub> C≡CNa	24
CH <sub>3</sub> S(O)CH <sub>3</sub> + NaH	CH <sub>3</sub> S(O)CH <sub>2</sub> Na	37
C <sub>6</sub> H <sub>5</sub> S(O)CH <sub>3</sub> + KH	C <sub>6</sub> H <sub>5</sub> S(O)CH <sub>2</sub> K	38
RC(=O)CH <sub>3</sub> + NaH	RC(=O)CH <sub>2</sub> Na	39
+ (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CK	RC(=O)CH <sub>2</sub> K	39
C <sub>6</sub> H <sub>5</sub> C(=O)CH <sub>3</sub> + [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> NNa	C <sub>6</sub> H <sub>5</sub> C(=O)CH <sub>2</sub> Na	40
CH <sub>3</sub> C(=O)CH <sub>3</sub> + KH/n-C <sub>4</sub> H <sub>9</sub> Li <sup>p</sup>	MCH <sub>2</sub> C(=O)CH <sub>2</sub> M <sup>q</sup>	41
9-C <sub>13</sub> H <sub>9</sub> CO <sub>2</sub> CH <sub>3</sub> <sup>r</sup> + KOCH <sub>3</sub>	(9-C <sub>13</sub> H <sub>8</sub> CO <sub>2</sub> CH <sub>3</sub> )K <sup>s</sup>	42
CH <sub>2</sub> Br <sub>2</sub> + [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> NNa	CH(Na)Br <sub>2</sub>	43
CH <sub>3</sub> CH(Cl)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> + [(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> NNa	CH <sub>3</sub> C(Na)(Cl)CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	44

<sup>a</sup> Example: 2-sodiotricyclo[2.2.1.0<sup>2,6</sup>]heptane is produced from tricyclo[2.2.1.0<sup>2,6</sup>]heptane.<sup>b</sup> Example: 10-camphenylsodium is produced from camphene (2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane).<sup>c</sup> n-C<sub>4</sub>H<sub>9</sub>K is prepared in situ from n-C<sub>4</sub>H<sub>9</sub>Li and KOR [R = C(CH<sub>3</sub>)<sub>3</sub>, menthyl].<sup>d</sup> Ferrocene.<sup>e</sup> The base is activated with a tertiary amine.<sup>f</sup> 1,1'-Dimetalloferrocene<sup>g</sup> M = Na, K, Cs; various dialkylamides are used, e.g., (i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>NM.<sup>h</sup> M = Na, K, Rb, Cs.<sup>j</sup> M = Na, K; the base is activated with a cryptand.<sup>i</sup> The base is activated with 18-crown-6<sup>k</sup> Sodium naphthalene radical anion<sup>l</sup> The reaction is run in hexamethylphosphoramide (HMPA).<sup>m</sup> Cyclopentadiene<sup>n</sup> Disodium dianion dimer of α-methylstyrene<sup>o</sup> Cyclopentadienylsodium.<sup>p</sup> Sequential treatment with KH then n-C<sub>4</sub>H<sub>9</sub>Li and tetramethylethylenediamine (TMED)<sup>q</sup> Mixed Li, K dianion.<sup>r</sup> 9-Carbomethoxyfluorene.<sup>s</sup> 9-Carbomethoxyfluorenylpotassium.

MH are used to prevent addition of the base to the electrophile. Simple alkyl and aryl group-IA organometallics cannot be used.

Acidic hydrocarbons ( $\text{p}K_{\text{a}} < 15$ ), such as malonic esters and  $\beta$ -diketones, are metallated by alkoxides in alcohol or by MH in ethers<sup>10</sup>.

Multiple metallations are the most common method of synthesizing di- or poly-metallated species<sup>11</sup>. Alkenes give polyanions with the mixed base,  $\text{C}_4\text{H}_9\text{Li}-(\text{CH}_3)_3\text{COK}$ . Ketones and  $\beta$ -diketones give mixed metal dianions or polyanions by sequential treatment with KH and  $\text{C}_4\text{H}_9\text{Li}$ .

Group-IA organometallics are formed by metallation (see Table 2).

(M. E. NEWCOMB)

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#### 5.5.3.3.2. by Metal–Metal Exchange with Less Active Organometallics.

Group-IA organometallics can react with other organometallics in a metal–metal exchange:



In the most useful synthetic applications of Eq. (a) (see Table 1), the reaction of commercially available organolithiums and group-IA alkoxides gives solid group-IA organometallics that contain little Li or solutions of group-IA organometallics that are highly reactive in metallation (see §5.5.3.3.1). The reaction is driven by the affinity of Li for oxygen.

TABLE 1. GROUP-IA ORGANOMETALLICS FROM METAL–METAL EXCHANGE

Reaction	Product	Refs.
$n\text{-C}_4\text{H}_9\text{Na} + (\text{C}_6\text{H}_5)_2\text{Hg}$	$\text{C}_6\text{H}_5\text{Na}$	1
$\text{ArCH}_2\text{Sn}(\text{C}_4\text{H}_9)_3 + n\text{-C}_4\text{H}_9\text{M}$	$\text{ArCH}_2\text{M}^a$	2
$(\text{CH}_3)_3\text{COM} + \text{RLi}$	$\text{RM}^b$	3,4
$(\text{CH}_3)_3\text{CONa} + \text{C}_2\text{H}_5\text{Li}$	$\text{C}_2\text{H}_5\text{Na}^c$	5
$(\text{CH}_3)_3\text{COK} + \text{CH}_3\text{Li}$	$\text{CH}_3\text{K}^c$	6
$(\text{CH}_3)_3\text{COM} + \text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Li}$	$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{M}^d$	7
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{ONa} + (\text{CH}_3)_3\text{CCH}=\text{CHCH}_2\text{Li}$	$(\text{CH}_3)_3\text{CCH}=\text{CHCH}_2\text{Na}^c$	8
$\text{ROK}^e + \text{C}_6\text{H}_5\text{CH}=\text{CHCH}(\text{Li})\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}(\text{K})\text{C}_6\text{H}_5$	9

<sup>a</sup> M = Na, K; Ar = 1-naphthyl, 2-naphthyl.

<sup>b</sup> M = Na, K, Cs; R =  $n\text{-C}_4\text{H}_9$ ,  $n\text{-C}_8\text{H}_{17}$ ,  $n\text{-C}_{12}\text{H}_{25}$ .

<sup>c</sup> The group-IA organometallic is isolated as a solid.

<sup>d</sup> M = Na, K, Cs.

<sup>e</sup> R = menthyl.

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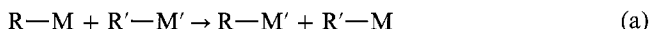


5.5. Formation of Bonds between Elements of Groups IVB and IA 175  
 5.5.3. Carbon-Group-IA Bonds  
 5.5.3.3. from Other Group-IA Organometallics of the Same Metal

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5.5.3.3.2. by Metal-Metal Exchange with Less Active Organometallics.

Group-IA organometallics can react with other organometallics in a metal-metal exchange:



In the most useful synthetic applications of Eq. (a) (see Table 1), the reaction of commercially available organolithiums and group-IA alkoxides gives solid group-IA organometallics that contain little Li or solutions of group-IA organometallics that are highly reactive in metallation (see §5.5.3.3.1). The reaction is driven by the affinity of Li for oxygen.

TABLE 1. GROUP-IA ORGANOMETALLICS FROM METAL-METAL EXCHANGE

Reaction	Product	Refs.
$n\text{-C}_4\text{H}_9\text{Na} + (\text{C}_6\text{H}_5)_2\text{Hg}$	$\text{C}_6\text{H}_5\text{Na}$	1
$\text{ArCH}_2\text{Sn}(\text{C}_4\text{H}_9)_3 + n\text{-C}_4\text{H}_9\text{M}$	$\text{ArCH}_2\text{M}^a$	2
$(\text{CH}_3)_3\text{COM} + \text{RLi}$	$\text{RM}^b$	3,4
$(\text{CH}_3)_3\text{CONa} + \text{C}_2\text{H}_5\text{Li}$	$\text{C}_2\text{H}_5\text{Na}^c$	5
$(\text{CH}_3)_3\text{COK} + \text{CH}_3\text{Li}$	$\text{CH}_3\text{K}^c$	6
$(\text{CH}_3)_3\text{COM} + \text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Li}$	$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{M}^d$	7
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{ONa} + (\text{CH}_3)_3\text{CCH}=\text{CHCH}_2\text{Li}$	$(\text{CH}_3)_3\text{CCH}=\text{CHCH}_2\text{Na}^c$	8
$\text{ROK}^e + \text{C}_6\text{H}_5\text{CH}=\text{CHCH}(\text{Li})\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}(\text{K})\text{C}_6\text{H}_5$	9

<sup>a</sup> M = Na, K; Ar = 1-naphthyl, 2-naphthyl.

<sup>b</sup> M = Na, K, Cs; R =  $n\text{-C}_4\text{H}_9$ ,  $n\text{-C}_8\text{H}_{17}$ ,  $n\text{-C}_{12}\text{H}_{25}$ .

<sup>c</sup> The group-IA organometallic is isolated as a solid.

<sup>d</sup> M = Na, K, Cs.

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- 176      5.5. Formation of Bonds between Elements of Groups IVB and IA  
           5.5.3. Carbon-Group-IA Bonds  
           5.5.3.3. from Other Group-IA Organometallics of the Same Metal

#### 5.5.3.3.3. by Addition to Olefins and Acetylenes.

Group-IA organometallics can add across a carbon-carbon multiple bond to give new organometallic species (see Table 1). The reaction is synthetically useful only when the new organometallic is stabilized. Addition to 1,1-diarylethylenes gives substituted diarylmethyl organometallics. Similarly, additions to 9-alkylidenefluorenes gives fluorenyl organometallics. Additions of group-IA organometallics to alkynes and arenes are known.

Addition is of limited utility because the new organometallic can compete with the original one for remaining electrophile to give polymeric products; anionic polymerization by such a sequence is well known<sup>1</sup>. However, when a weak acid is present, monoadducts of group-IA organometallics with olefins can be trapped (see Table 1). Metallation of an olefin to give allylic or vinyl organometallics is another competing reaction<sup>2</sup> (see §5.5.3.3.1).

TABLE 1. GROUP-IA ORGANOMETALLICS FORMED BY ADDITION OF ORGANOMETALLICS TO C—C MULTIPLE BONDS<sup>a</sup>.

Reaction	Product	Ref.
$\text{PhC}(\text{CH}_3)_2\text{K} + \text{Ph}_2\text{C}=\text{CH}_2$	$\text{PhC}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{Ph})_2\text{K}$	2
$n\text{-C}_5\text{H}_{11}\text{Na} + \text{Ph}_2\text{C}=\text{CH}_2$	$(n\text{-C}_5\text{H}_{11})\text{CH}_2\text{C}(\text{Ph})_2\text{Na}$	3
$\text{PhC}(\text{CH}_3)_2\text{K} + 9\text{-(PhCH=)}\text{C}_{13}\text{H}_8^b$	$9\text{-}[\text{PhC}(\text{CH}_3)_2\text{CHPh}]\text{C}_{13}\text{H}_8\text{K}$	2
$\text{PhC}(\text{CH}_3)_2\text{K} + \text{PhC}\equiv\text{CR}^c$	$\text{PhC}(\text{CH}_3)_2\text{C}(\text{R})=\text{C}(\text{K})\text{Ph}$	4
$\text{PhC}(\text{CH}_3)_2\text{K} + \text{C}_{14}\text{H}_{10}^d$	$10\text{-}[\text{PhC}(\text{CH}_3)_2]\text{-9-K-C}_{14}\text{H}_{10}^e$	5
$\text{C}_6\text{H}_5\text{K} + \text{C}_6\text{H}_6$	$\text{Ph-C}_6\text{H}_5\text{K}^f$	6
$\text{PhC}(\text{CH}_3)_2\text{K} + \text{H}_2\text{C}=\text{CH}_2$	$\text{PhC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{K}^g$	4
$\text{Ph}_3\text{CNa} + \text{CH}_2=\text{CHCH}=\text{CH}_2$	$\text{Ph}_3\text{CCH}_2\text{CH}=\text{CHCH}_2\text{Na}^h$	7

<sup>a</sup> Ph = C<sub>6</sub>H<sub>5</sub>.

<sup>b</sup> 9-Benzalfluorene.

<sup>c</sup> R = CH<sub>3</sub>, Ph.

<sup>d</sup> Anthracene.

<sup>e</sup> 10-(2-Phenyl-2-methylethyl)-9-potassio-9,10-dihydroanthracene.

<sup>f</sup> Addition is followed by metallation to give 1,4-dipotassio-1,4-dihydrobiphenyl. The reaction with PhNa fails.

<sup>g</sup> The transient organometallic product is protonated by ether.

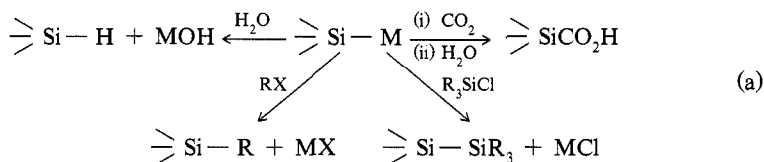
<sup>h</sup> The transient organometallic product is protonated by dicyclohexylamine.

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### 5.5.4. Silicon–Group-IA Bonds

Organosilylmetallics of group IA are formed and studied in solution. Formation of solutions of Si–alkali metal bonds<sup>1,2</sup> is performed under an inert atmosphere (N<sub>2</sub> or Ar), under moisture and O<sub>2</sub>-free conditions and in solvents that are dried before use. Storage of the reagents is sometimes possible, preferably in the cold, but reaction with solvent frequently occurs, and aged samples contain decreased amounts of silylmetallic. The yield of active silylmetallic may be determined for freshly prepared solutions from acid titration of the MOH generated from aqueous hydrolysis of the Si–M bond. However, because some methods involve concomitant formation of metal alkoxides, a double-titration method<sup>3</sup> involving reaction of an aliquot with an organic bromide (allyl bromide gives the most consistent results) prior to hydrolysis to determine the LiOR content is used in addition to the determination of the total active Li content from hydrolysis of another aliquot. This analysis usually is not performed, however, and the minimum yield of the reagent must be inferred from a trapping reaction. The trapping reactions include coupling with an organic halide or silyl chloride, carbonation to the acid or isolation of the hydrosilane formed on hydrolysis:



Solid silylmetallic reagents can be isolated. Evaporation of liq NH<sub>3</sub> affords solid reagents<sup>4</sup>, such as Et<sub>3</sub>GeK; pure, solid Me<sub>3</sub>SiLi is prepared by vacuum sublimation<sup>5</sup> and (Me<sub>3</sub>Si)<sub>3</sub>SiLi·3 THF (tetrahydrofuran) may be recrystallized from pentane<sup>6</sup> and Li(SiPh<sub>2</sub>)<sub>4</sub>Li·2 THF from cyclohexane<sup>7</sup>. Crystalline 1:1 adducts, e.g., Et<sub>3</sub>SiLi·L, are formed by addition of hexamethylphosphoramide (HMPA), tetramethylethylenediamine (TMED), or 1,2-dimethoxyethane (DME) to Et<sub>3</sub>SiLi in hexane. Solid Me<sub>3</sub>SiLi·DME is also known<sup>8</sup>. Isolation of KSiH<sub>3</sub>, free of solvent and KH is also possible<sup>9</sup>.

(J. Y. COREY)

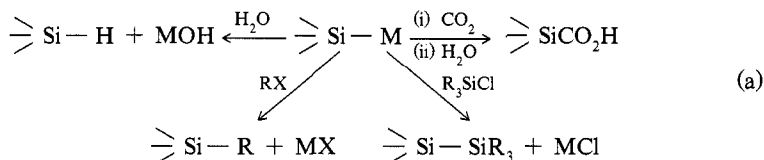
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#### 5.5.4.1. from the Elements.

The alkali metals react with elemental Si at elevated T in an inert atmosphere. At least two distinct compositions form from the reaction of Li and Si. When Li and Si are heated in Ni crucibles at a ratio of 2Li:Si, Li<sub>2</sub>Si is formed at ca. 530°C; at a ratio of 4

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Li: Si  $\text{Li}_4\text{Si}$  is formed, but at a higher T (ca.  $630^\circ\text{C}$ )<sup>1</sup>. Lithium and Si also react near the mp of Li ( $185\text{--}200^\circ\text{C}$ ), and  $\text{Li}_{4n}\text{Si}_n$  (probably  $\text{Li}_4\text{Si}$ ) is the only product<sup>2</sup>. The phase diagram of Li and Si using closed Mo crucibles shows<sup>2</sup> both  $\text{Li}_{4n}\text{Si}_n$  and  $\text{Li}_{2n}\text{Si}_n$ , whereas support for  $\text{Li}_2\text{Si}$ ,  $\text{Li}_{10}\text{Si}_3$  and  $\text{Li}_{17}\text{Si}_2$  is claimed for the Li–Si system<sup>3</sup>. Reaction of elemental Li and Si in Ta ampules at 1270 K provides  $\text{Li}_{12}\text{Si}_7$ , a semiconductor<sup>4</sup>.

When Si is heated with an excess of the other alkali metals, only MSi is formed. When Si and xs Na are heated at  $700^\circ\text{C}$  in a sealed Fe bomb for 1–2 days, NaSi is formed and KSi is formed at  $650^\circ\text{C}$ , but 4–5 days and a special apparatus are required<sup>5</sup>. The compounds RbSi and CsSi are formed at  $600^\circ\text{C}$ . The formation<sup>6</sup> of KSi, RbSi and CsSi results from using specially designed equipment.

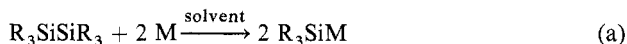
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### 5.5.4.2. from Organodi- and Organopolysilanes

#### 5.5.4.2.1. with Alkali Metals.

(i) Disilanes. The silylmetallics form from Si—Si-bonded reagents and alkali metals:



Two moles of silylmetallic form per mole of disilane, and the reagent obtained is salt free, but the disilane (or polysilane) must be prepared from a halosilane, which is the commercially available reagent. For a direct route from chlorosilane to silylmetallic through the disilane, which is not isolated, see §5.5.4.3.

As a practical method Eq. (a) is limited to disilanes that contain one aryl group per Si. The most common solvent is tetrahydrofuran (THF). The disilane–metal mixture is added in a small quantity of solvent (enough to make a paste); this is stirred until the reaction is initiated as evidenced by a color change, after which the remainder of the solvent is added dropwise and stirring continued until the disilane dissolves<sup>1</sup>. The resultant silylmetallic is soluble in THF and stable at RT. Decomposition occurs on prolonged reflux owing to reaction with the solvent<sup>2</sup>. Cleavage of the Si–Si bond occurs more slowly in tetrahydropyran (THP) or 1,4-dioxane (72 h in the former), but the silylmetallic is soluble and solutions are more stable<sup>3,4</sup> than those in THF. Ethylene glycol dimethyl ether promotes disilane cleavage as effectively as THF, but the resulting silylmetallic is less stable<sup>4</sup>. Diethyl ether may be employed also, but the silylmetallic is insoluble in this solvent<sup>5</sup>. Although these observations are primarily for preparation of  $\text{Ph}_3\text{SiM}$  in solution, the results are general. The Si—Si bond is cleaved readily by Li metal in THF but more slowly by Na, in which case addition of catalytic quantities of

Li: Si  $\text{Li}_4\text{Si}$  is formed, but at a higher T (ca.  $630^\circ\text{C}$ )<sup>1</sup>. Lithium and Si also react near the mp of Li ( $185\text{--}200^\circ\text{C}$ ), and  $\text{Li}_{4n}\text{Si}_n$  (probably  $\text{Li}_4\text{Si}$ ) is the only product<sup>2</sup>. The phase diagram of Li and Si using closed Mo crucibles shows<sup>2</sup> both  $\text{Li}_{4n}\text{Si}_n$  and  $\text{Li}_{2n}\text{Si}_n$ , whereas support for  $\text{Li}_2\text{Si}$ ,  $\text{Li}_{10}\text{Si}_3$  and  $\text{Li}_{17}\text{Si}_2$  is claimed for the Li-Si system<sup>3</sup>. Reaction of elemental Li and Si in Ta ampules at  $1270\text{ K}$  provides  $\text{Li}_{12}\text{Si}_7$ , a semiconductor<sup>4</sup>.

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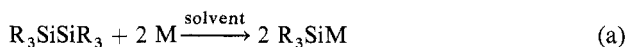
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(i) Disilanes. The silylmetallics form from Si—Si-bonded reagents and alkali metals:



Two moles of silylmetallic form per mole of disilane, and the reagent obtained is salt free, but the disilane (or polysilane) must be prepared from a halosilane, which is the commercially available reagent. For a direct route from chlorosilane to silylmetallic through the disilane, which is not isolated, see §5.5.4.3.

As a practical method Eq. (a) is limited to disilanes that contain one aryl group per Si. The most common solvent is tetrahydrofuran (THF). The disilane-metal mixture is added in a small quantity of solvent (enough to make a paste); this is stirred until the reaction is initiated as evidenced by a color change, after which the remainder of the solvent is added dropwise and stirring continued until the disilane dissolves<sup>1</sup>. The resultant silylmetallic is soluble in THF and stable at RT. Decomposition occurs on prolonged reflux owing to reaction with the solvent<sup>2</sup>. Cleavage of the Si-Si bond occurs more slowly in tetrahydropyran (THP) or 1,4-dioxane (72 h in the former), but the silylmetallic is soluble and solutions are more stable<sup>3,4</sup> than those in THF. Ethylene glycol dimethyl ether promotes disilane cleavage as effectively as THF, but the resulting silylmetallic is less stable<sup>4</sup>. Diethyl ether may be employed also, but the silylmetallic is insoluble in this solvent<sup>5</sup>. Although these observations are primarily for preparation of  $\text{Ph}_3\text{SiM}$  in solution, the results are general. The Si—Si bond is cleaved readily by Li metal in THF but more slowly by Na, in which case addition of catalytic quantities of

biphenyl or naphthalene considerably shortens the reaction period and improves the yield<sup>6</sup>. Cleavage of the Si—Si bond by Na dispersion in dioxane or 40 % Na amalgam in Et<sub>2</sub>O does not occur<sup>5</sup>. Sodium—potassium alloy reacts with Si—Si bonds to give the silylpotassium in 1,2-dimethoxyethane (DME), but cleavage of the solvent occurs at RT within a day<sup>7</sup>. Silylpotassium reagents may also be formed in ether<sup>5</sup>, and xs alloy is removed by addition of Hg.

Cleavage of Si—Si bonds in MePh<sub>2</sub>SiSiPh<sub>2</sub>Me by Li<sup>1</sup> or Na<sup>6</sup> metal in THF occurs to give good yields of MePh<sub>2</sub>SiLi(Na), but catalytic quantities of biphenyl must be added to the latter. Additional replacement of phenyl substituents by methyl (or ethyl) in the starting disilane, R<sub>2</sub>PhSiSiPhR<sub>2</sub>, gives R<sub>2</sub>PhSiLi (R = Me, Et), but the reagent decomposes in THF more rapidly than either MePh<sub>2</sub>SiLi or Ph<sub>3</sub>SiLi<sup>1,7</sup>. Reaction of Me<sub>2</sub>PhSiSiPhMe<sub>2</sub> with Na metal in THF even in the presence of biphenyl gives no useful silylsodium intermediate<sup>6</sup>. The formation of R<sub>2</sub>PhSiLi (R = i-Pr, PhCH<sub>2</sub>), from the disilane precursor and Li metal in aromatic and ether solvents occurs<sup>8</sup>.

Solutions of the silyllithiums Ph<sub>3</sub>SiLi, MePh<sub>2</sub>SiLi and Me<sub>2</sub>PhSiLi suitable for kinetic studies may be prepared under vacuum<sup>9</sup>.

The formation of trialkylsilyllithiums by cleavage of Si—Si bonds does not have practical utility, in part owing to reaction with solvent. After 2 weeks, 30 % cleavage of Me<sub>3</sub>SiSiMe<sub>3</sub> occurs over a Li film, but analysis of the solution shows<sup>9</sup> that the ratio of Me<sub>3</sub>SiLi to LiO(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub> is 1 : 10. Even when a solvent is employed in which Li is soluble, such as hexamethylphosphoramide (HMPA), the R<sub>3</sub>SiLi (R = n-Bu) formed attacks the solvent too rapidly to be useful as a synthetic procedure<sup>10</sup>.

Cleavage of unsymmetrical disilanes is expected to give two silyllithiums and may be practical only where the two are easily distinguished. The optically active disilane, (–)-neo-C<sub>5</sub>H<sub>11</sub>PhMeSiSiMePh<sub>2</sub>, generates solutions that contain optically stable neo-C<sub>5</sub>H<sub>11</sub>PhMeSiLi from Li metal in THF<sup>11</sup>. The formation of Et<sub>3</sub>SiLi involves reaction of Et<sub>3</sub>SiGePh<sub>3</sub> with Li metal in EtNH<sub>2</sub>, but the two organometallic reagents cannot be separated<sup>12</sup>. Low yields of Me<sub>3</sub>SiK are formed<sup>13</sup> from Ph<sub>3</sub>SiSiMe<sub>3</sub> and Na-K alloy in Et<sub>2</sub>O.

Disilanes with functional groups, such as Ph<sub>2</sub>HSiSiHPh<sub>2</sub>, react with Li metal in THF, but the Li reagent, Ph<sub>2</sub>SiHLi, undergoes further reaction with starting material<sup>14</sup>. Silyllithium reagents with Si functional groups and polymetallic reagents are rare.

The cleavage of Si—Si bonds as a function of substituent, metal and solvent are illustrated in Table 1.

(ii) **Organopolysilanes.** Cleavage of Si—Si bonds in organopolysilanes also occurs but is not always discriminating, and mixtures of silylmetallics are formed. The best results are obtained with phenyl or silyl substituents. Polysilanes with Me substituents give the most reactive disilanes species, but mixtures of metallic reagents are obtained.

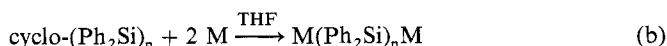
Although only one Si—Si bond in (Me<sub>3</sub>Si)<sub>4</sub>Si is cleaved by Li or Na in THF in the presence of catalytic amounts of biphenyl<sup>15</sup>, the preferential method of preparation of (Me<sub>3</sub>Si)<sub>3</sub>SiLi is described in §5.5.4.2.2. Linear trisilanes provide two organosilylmetallic reagents if all substituents are identical. The trisilane Ph<sub>3</sub>Si(SiPh<sub>2</sub>)SiPh<sub>3</sub> reacts with Li metal in THF to give a mixture of Ph<sub>3</sub>SiLi and Ph<sub>5</sub>Si<sub>2</sub>Li in good yields<sup>16</sup>. However, the unsymmetrical trisilane Ph<sub>3</sub>SiSiMe<sub>2</sub>SiPh<sub>3</sub>, which might be expected to give Ph<sub>3</sub>SiSiMe<sub>2</sub>Li, gives<sup>17</sup> only Ph<sub>3</sub>SiLi and (Me<sub>2</sub>Si)<sub>6</sub>. For other routes to disilanylithiums, see §5.5.4.2.3. The linear silane, Me<sub>10</sub>Si<sub>4</sub>, gives<sup>18</sup> mixtures of silylpotassiums with Na-K alloy in THF.

TABLE 1. CLEAVAGE OF SILICON-SILICON BONDS BY ALKALI METALS

Silyl metallic	Starting <sup>a</sup> polysilane (mmol)	Solvent (mL) <sup>b</sup>	Time (h), T (°C)	Yield, %	Method of yield determination <sup>c</sup>	Ref.
Ph <sub>3</sub> SiLi	Ph <sub>6</sub> Si <sub>2</sub> (29)	THF (150)	3, RT	79	Me <sub>3</sub> SiCl	1
			24, Δ	6	Me <sub>3</sub> SiCl	1
	Ph <sub>6</sub> Si <sub>2</sub> (25)	THP (135)	72, RT	81	Ph <sub>3</sub> SiCl	3
Ph <sub>3</sub> SiNa	Ph <sub>6</sub> Si <sub>2</sub> (25)	THF (100) <sup>d</sup>	5, RT	94	Double titration	6
				83	H <sub>2</sub> O	6
		DME (35)	37, RT	71	Double titration	27
Ph <sub>3</sub> SiK	Ph <sub>6</sub> Si <sub>2</sub> (9.7)	DME (35)	2.2, RT	77	Me <sub>3</sub> SiCl	27
			32, RT	38	Me <sub>3</sub> SiCl	27
	Ph <sub>6</sub> Si <sub>2</sub> (7.7)	Et <sub>2</sub> O (60)	20.5, RT	53	Ph <sub>2</sub> SiCl <sub>2</sub>	28
	Ph <sub>6</sub> Si <sub>2</sub> (10)	Et <sub>2</sub> O (50)	25, RT	86	Me <sub>3</sub> SiCl	29
(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiK	(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Si <sub>2</sub> (5.0)	Et <sub>2</sub> O (75)	57, RT	56	CO <sub>2</sub>	30
Ph <sub>3</sub> SiRb	Ph <sub>6</sub> Si <sub>2</sub> (5)	n-Bu <sub>2</sub> O (25)	30, 90	48	Me <sub>3</sub> SiCl	29
Ph <sub>3</sub> SiCs	Ph <sub>6</sub> Si <sub>2</sub> (2.9)	Et <sub>2</sub> O (13)	24, RT	52	Me <sub>3</sub> SiCl	29
Ph <sub>2</sub> MeSiLi	(Ph <sub>2</sub> MeSi) <sub>2</sub> (13)	THF (70)	1, RT	74	Me <sub>3</sub> SiCl	1
				9.5	Ph <sub>3</sub> SiCl	
Ph <sub>2</sub> MeSiNa	(Ph <sub>2</sub> MeSi) <sub>2</sub> (25)	THF (100)	5, RT	71	H <sub>2</sub> O	6
Ph <sub>2</sub> HSiLi	(Ph <sub>2</sub> HSi) <sub>2</sub>	THF			Ph <sub>3</sub> SiCl	14
Ph(i-Pr) <sub>2</sub> SiLi	[Ph(i-Pr) <sub>2</sub> Si] <sub>2</sub> (0.6)	C <sub>6</sub> H <sub>6</sub> (2)	> 3, RT	100	Acid titration	8
PhEt <sub>2</sub> SiLi	(PhEt <sub>2</sub> Si) <sub>2</sub> (15)	THF (21)	18.5, RT	40	Ph <sub>3</sub> SiCl	7
Me <sub>3</sub> SiLi	Me <sub>6</sub> Si <sub>2</sub> <sup>d</sup>	THF		0	No reaction	20
(Me <sub>3</sub> Si) <sub>3</sub> SiLi	[(Me <sub>3</sub> Si) <sub>3</sub> Si] <sub>2</sub> (2)	THF (6)	1.5, RT	e		31
Ph <sub>2</sub> Si <sub>2</sub> Li <sup>f</sup>	Ph <sub>8</sub> Si <sub>3</sub> (5)	THF (20)	3, RT	77	H <sub>2</sub> O	16
Li(SiPh <sub>2</sub> ) <sub>4</sub> Li	(Ph <sub>2</sub> Si) <sub>2</sub> (11)	THF (20)	3, RT	27	Me <sub>3</sub> PO <sub>4</sub>	19
	(Ph <sub>2</sub> Si) <sub>4</sub> (14)	THF (35)	14, RT	33	Ph <sub>2</sub> SiCl <sub>2</sub>	22
Li(SiPh <sub>2</sub> ) <sub>5</sub> Li	(Ph <sub>2</sub> Si) <sub>5</sub> (16)	THF (160)	2, RT	100	Double titration	23
				76	Me <sub>3</sub> PO <sub>4</sub>	23
Na(SiPh <sub>2</sub> ) <sub>4</sub> Na	(Ph <sub>2</sub> Si) <sub>5</sub> <sup>d</sup>	THF		50-70	Me <sub>3</sub> SiCl	20
Li(SiPh <sub>2</sub> ) <sub>6</sub> Li	(Ph <sub>2</sub> Si) <sub>6</sub> (12)	THF (120)	4, RT	g	Me <sub>3</sub> PO <sub>4</sub>	25

<sup>a</sup> Excess metal used except for cyclic polysilanes. Potassium derivatives prepared from Na-K alloy.<sup>b</sup> Tetrahydropyran (THP).<sup>c</sup> Reagent indicated is added and % yield corresponds to coupling product when chlorosilanes or Me<sub>3</sub>PO<sub>4</sub> are added, to isolated silane when H<sub>2</sub>O is added and to active silylmatalic from double titration directly.<sup>d</sup> Biphenyl added.<sup>e</sup> Yield not specified; (Me<sub>3</sub>Si)<sub>3</sub>SiH and (Me<sub>3</sub>Si)<sub>4</sub>Si are major hydrolysis products.<sup>f</sup> Mixed with Ph<sub>3</sub>SiLi<sup>g</sup> Product isolated in greatest % yield is the trisilane, Me(SiPh<sub>2</sub>)<sub>3</sub>Me

Cyclic organopolysilanes are cleaved by Li (or Na) metal in THF to give  $\alpha,\omega$ -dilithio or disodio reagents:



The results are a function of the ring size<sup>19-24</sup>. The highest yields of dimetallo reagent are obtained from the cyclopentasilane with both Li<sup>23</sup> and Na<sup>29</sup> metal<sup>20</sup>. Conversions to the disodio reagent are improved<sup>20</sup> by addition of biphenyl or naphthalene for  $n = 4$  or  $5$ . The disproportionation of Li(SiPh<sub>2</sub>)<sub>6</sub>Li to mixtures of dilithio reagents occurs rapidly, so reaction (b) is not a viable approach to 1,6-dilithiopolsilanes<sup>24,25</sup>. Solid Li(SiPh<sub>2</sub>)<sub>4</sub>Li·2 THF<sup>24,25</sup> can be recrystallized from cyclohexane<sup>26</sup>.



Although cyclo-(Me<sub>2</sub>Si)<sub>6</sub> is also cleaved by Li in the presence of biphenyl, mixtures of dilithio species are formed<sup>20</sup>, and mixtures of dipotassium species are formed<sup>21</sup> from (Me<sub>2</sub>Si)<sub>6</sub> and Na–K alloy in THF.

(J. Y. COREY)

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#### 5.5.4.2.2. with Anionic Reagents.

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The preferred method for (Me<sub>3</sub>Si)<sub>3</sub>SiLi is treatment of (Me<sub>3</sub>Si)<sub>4</sub>Si with MeLi–LiBr. The solid reagent may be isolated and purified (in 92% yield)<sup>7</sup>. The same organolithium reagent is also formed<sup>8</sup> from (Me<sub>3</sub>Si)<sub>6</sub>Si<sub>2</sub> acting as a disilane and MeLi in THF. Ring opening of cyclopolysilanes with MeLi gives a monolithium reagent; e.g., (Ph<sub>2</sub>Si)<sub>4</sub> with MeLi gives<sup>9</sup> MePh<sub>2</sub>Si(SiPh<sub>2</sub>)<sub>2</sub>SiPh<sub>2</sub>Li.

5.5. Formation of Bonds between Elements of Groups IVB and IA 181  
 5.5.4. Silicon-Group-IA Bonds  
 5.5.4.2. from Organodi- and Organopolysilanes

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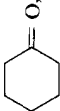
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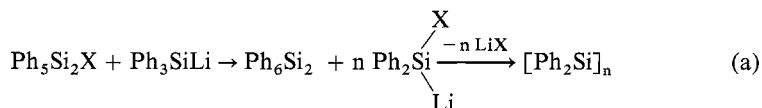
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TABLE 1. CLEAVAGE OF SILICON-SILICON BONDS BY METAL SALTS AND ORGANOMETALLIC REAGENTS

Silylmetallic	Silane precursor (mmol)	Metal salt or RLi (mmol)	Solvent <sup>a</sup> (mL), time (h), T (°C)	Yield, %	Method of determination <sup>b</sup>	Refs.
Ph <sub>3</sub> SiLi	Ph <sub>3</sub> Si <sub>2</sub> (1 equiv)	PhLi (10 equiv)	THF (—, 24, RT)	89	<sup>c</sup>	14
Me <sub>3</sub> SiLi	Me <sub>6</sub> Si <sub>2</sub> (2.5)	MeLi (2)	HMPA (2, 0.25, 0)	99		1
Me <sub>3</sub> SiNa	Me <sub>6</sub> Si <sub>2</sub> (1 equiv)	NaOMe (1 equiv)	HMPA (—, < 0.1, RT)	44–57	PhBr <sup>d</sup>	2
		Na	HMPA	0		2
Me <sub>3</sub> SiK	Me <sub>6</sub> Si <sub>2</sub> (20)	NaOMe (10)	DMI <sup>a</sup> (10, 1, RT)	100	C <sub>3</sub> H <sub>11</sub> Cl	15
	Me <sub>6</sub> Si <sub>2</sub> (1.8)	KOMe (0.2) <sup>e</sup>	HMPA (10, 0.1, RT)	100	Epoxides	3
	Me <sub>6</sub> Si <sub>2</sub> (10)	KH (20)	HMPA (—, 0.1, 30–40)	80	Ph <sub>3</sub> GeBr	4
	Me <sub>6</sub> Si <sub>2</sub> (7.5)	KOMe (7.5)	THF (14, —, RT)	88	C <sub>3</sub> H <sub>7</sub> Cl	15
Me <sub>2</sub> (MeO)SiNa	(MeO) <sub>2</sub> Me <sub>2</sub> Si <sub>2</sub> (20)	NaOMe (20)	THF (—, 2, RT)	80	PhBr	6
Me(MeO) <sub>2</sub> SiNa	(MeO) <sub>4</sub> Me <sub>2</sub> Si <sub>2</sub> (20)	NaOMe (20)	THF (—, 24, RT)	90	PhBr	6
(Me <sub>3</sub> Si) <sub>2</sub> SiLi	(Me <sub>3</sub> Si) <sub>4</sub> Si (180)	MeLi–LiBr (180)	THF–Et <sub>2</sub> O <sup>f</sup> (900, 12, RT)	92		7
(Me <sub>2</sub> HSi) <sub>3</sub> SiLi	(Me <sub>2</sub> HSi) <sub>4</sub> Si	MeLi <sup>h</sup>	THF–Et <sub>2</sub> O	52	Me <sub>3</sub> PO <sub>4</sub>	16

<sup>a</sup> Solvent key: DMI, 1,3-dimethyl-2-imidazolidinone<sup>b</sup> The reagent indicated was added and the % yield of organometallic inferred from coupling product isolated.<sup>c</sup> Percent Ph<sub>3</sub>Si isolated.<sup>d</sup> No reaction<sup>e</sup> 18-Crown-6, 7.5 mmol, also present.<sup>f</sup> Volume ratio of the THF–Et<sub>2</sub>O = 8 : 1.<sup>g</sup> Isolated solid organometallic.<sup>h</sup> Equimolar in silane and MeLi.

Although not explored for formation of disilanyllithium reagents, an  $R_2Si$  unit can be removed from a cyclic polysilane by attack of a silyllithium. When  $(Ph_2Si)_6$  is treated with  $MePh_2SiLi$  in THF,  $MePh_4Si_2Li$  is produced in high yields because reaction with aq acid gives  $MePh_4Si_2H$  (95% crude)<sup>10</sup>. However, addition of  $Br(SiPh_2)_2Br$  gives mixtures of products possibly owing to metal-halogen exchange and condensation with the organosilanes thus formed. Similarly,  $Ph_5Si_2Li$  is formed from  $(Ph_2Si)_5$  and  $Ph_3SiLi$  in THF as evidenced from isolation of  $Ph_5Si_2H$  (57–63%) on hydrolysis<sup>11</sup>. Because Si—Si bonds are susceptible to attack by nucleophiles, the possibility of forming sila-functional metalics from disilanes is explored: but decomposition of the silylmetallic occurs by elimination of  $LiX$ <sup>12</sup>:



Trimethylsilyl anion<sup>13</sup>, free of metal ions, is generated when  $[n-Bu_4N]F$  is added to  $(Me_3Si)_2$  in HMPA.

Examples of Si—Si bond cleavage by metal salts and organometallic reagents are shown in Table 1.

(J. Y. COREY)

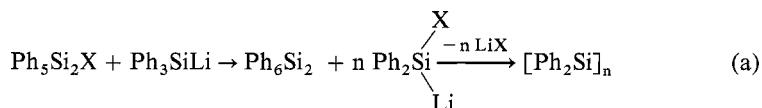
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#### 5.5.4.3. from Organohalosilanes with Alkali Metals.

The formation of silylmetallics by cleavage of Si—Si bonds with alkali metals is described in §5.5.4.2.1. Because Si—Si bonds can be formed by condensation of halosilanes with alkali metals, a direct route to silyl metalics should be possible by forming and reacting the disilane (or polysilane) with a metal without isolating the intermediate Si—Si-bonded species. However, this approach contains the same inherent restrictions as those described in §5.5.4.2.1; i.e., there must be one aryl group bonded to Si in the starting halosilane (see Table 1). Reaction of  $Ph_3SiCl$  does not occur with Na, but

5.5. Formation of Bonds between Elements of Groups IVB and IA 183  
 5.5.4. Silicon—Group-IA Bonds

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Trimethylsilyl anion<sup>13</sup>, free of metal ions, is generated when  $[n-Bu_4N]F$  is added to  $(Me_3Si)_2$  in HMPA.

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TABLE 1. REACTION OF HALOSILANES WITH ALKALI METALS

Silylmetallic	Halosilane (mmol)	M (g-at)	Solvent <sup>a</sup> (h)	Yield (%)	Method of determination <sup>b</sup>	Ref.
Ph <sub>3</sub> SiLi	Ph <sub>3</sub> SiF (25)	Li (100)	THF (3)	84	Me <sub>3</sub> SiCl	1
	Ph <sub>3</sub> SiCl (20)	Li (80)	THF (3)	90	Ph <sub>3</sub> SiCl	2
			THP (4)	64	Ph <sub>3</sub> SiCl	2
Ph <sub>3</sub> SiNa	Ph <sub>3</sub> SiCl	Na	THF	0	<sup>c</sup>	2
Ph <sub>3</sub> SiK	Ph <sub>3</sub> SiCl (20)	Na–K <sup>d</sup>	THF	75	Me <sub>3</sub> SiCl	2
	Ph <sub>3</sub> SiCl (15)	Na–K <sup>e</sup>	Et <sub>2</sub> O (3)	97	Me <sub>3</sub> SiCl	3
Ph <sub>3</sub> SiRb	Ph <sub>3</sub> SiCl (10)	Rb (3)	THF (3) <sup>f</sup>	69	Me <sub>3</sub> SiCl	2
Ph <sub>3</sub> SiCs	Ph <sub>3</sub> SiCl (10)	Cs (3)	THF (4) <sup>g</sup>	46	Me <sub>3</sub> SiCl	2
(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiK	(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCl (10)	Na–K	Et <sub>2</sub> O (24)	69	CO <sub>2</sub>	4
Ph <sub>2</sub> MeSiLi	Ph <sub>2</sub> MeSiCl (16.4)	Li (xs)	THF (30)	36	Ph <sub>3</sub> SiCl	5
Ph <sub>2</sub> HSiLi	Ph <sub>2</sub> HSiCl (59)	Li (146)	THF (100)	11	Ph <sub>3</sub> SiCl	6
t-BuPh <sub>2</sub> SiLi	t-BuPh <sub>2</sub> SiCl	Li	THF (6)	100	c-C <sub>6</sub> H <sub>11</sub> NCO	7
Ph(i-Pr) <sub>2</sub> SiLi	Ph(i-Pr) <sub>2</sub> SiCl (61)	Li (31)	THF (6)	70	D <sub>2</sub> O	8
Ph(PhCH <sub>2</sub> ) <sub>2</sub> SiLi	Ph(PhCH <sub>2</sub> ) <sub>2</sub> SiCl (9)	Li (190)	THF	88	D <sub>2</sub> O	8
PhMe <sub>2</sub> SiLi	PhMe <sub>2</sub> SiCl (21)	Li (100)	THF (3)	33	Ph <sub>3</sub> SiCl	2

<sup>a</sup> Solvent key: THF, tetrahydrofuran; THP, tetrahydropyran. Reactions at RT unless specified otherwise.

<sup>b</sup> Reagent indicated was added, and % yield corresponds to coupling product (halosilane), hydrosilane (D<sub>2</sub>O) or acid (CO<sub>2</sub>) formed.

<sup>c</sup> Ph<sub>6</sub>Si<sub>2</sub> isolated (46%).

<sup>d</sup> 2.5 mL alloy, Na : K = 1 : 4

<sup>e</sup> 2.0 mL alloy, Na : K = 1 : 4

<sup>f</sup> Reaction carried out with cooling (ice bath).

<sup>g</sup> Reaction carried out at –50°C.

with Rb and Cs metal the corresponding organometallics, Ph<sub>3</sub>SiRb and Ph<sub>3</sub>SiCs, are obtained<sup>2</sup>. Addition of Na metal to t-Bu<sub>3</sub>SiBr in THF provides<sup>9</sup> solvated t-Bu<sub>3</sub>SiNa (formulated as [Na(THF)<sub>4</sub>][Na{Si(Bu-t)<sub>3</sub>}<sub>2</sub>]). When (C<sub>6</sub>F<sub>5</sub>)Ph<sub>2</sub>SiCl is treated with Li metal in tetrahydrofuran (THF), no organometallic is obtained<sup>10</sup>. Extension of the method to halodisilanes, such as R<sub>3</sub>SiR<sub>2</sub>SiCl, is unlikely because Si—Si bond cleavage in the coupling product R<sub>3</sub>Si(SiR<sub>2</sub>)<sub>2</sub>SiR<sub>3</sub> is likely to give a mixture of silylmetallic reagents. The use of nucleophilic reagents, such as MOH, MOR, NH or RLi (see §5.5.4.2.2), leads to substitution at Si in the halosilanes.

Employing a hot-atom technique shows that SiCl<sub>4</sub> reacts with xs Li vapor to give SiLi<sub>4</sub>. Hydrolysis of the product gives SiH<sub>4</sub> (12%) and no disilane<sup>11</sup>.

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#### 5.5.4.4. from Organosilicon Hydrides with Alkali Metals and Metal Hydrides.

Reaction of hydrosilanes with alkali metals is seldom employed for generating silylmetallic reagents, except for  $\text{H}_3\text{SiM}$  ( $\text{M} = \text{Na}, \text{K}, \text{Pb}, \text{Cs}$ )<sup>1-4</sup>. The silylmetallics of K, Rb and Cs may be prepared and isolated<sup>1,2</sup> from 1,2-dimethoxyethane (DME) in 7-28 days<sup>4</sup>. The reaction of  $\text{SiH}_4$  and potassium in hexamethylphosphoramide (HMPA) (a carcinogen) gives<sup>3</sup> a high yield of  $\text{KSiH}_3$ , and Na and  $\text{SiH}_4$  react<sup>2</sup> in DME.

Triphenylsilane reacts with Na-K alloy in  $\text{Et}_2\text{O}$  (2 days, RT), and addition of PhBr gives  $\text{Ph}_4\text{Si}$  (in 67 % yield)<sup>5</sup>. However,  $\text{Ph}_2\text{SiH}_2$  gives<sup>6</sup>  $\text{Ph}_4\text{Si}$  (88 % based on the phenyl content of the starting silane) in the presence of Na-K, therefore, formation of  $\text{Ph}_3\text{SiK}$  from  $\text{Ph}_3\text{SiH}$ -Na-K is suspected.

The alkylsilane,  $\text{Et}_3\text{SiH}$ , does not react<sup>5</sup> with Na-K in  $\text{Et}_2\text{O}$ , and although  $\text{Et}_3\text{SiH}$  is converted to  $\text{Et}_3\text{SiNHet}$  in  $\text{EtNH}_2$  when catalytic quantities of Li metal are present, it is doubtful that  $\text{Et}_3\text{SiLi}$  is generated<sup>7</sup>. Apparently,  $(\text{Ph}_3\text{Ge})_3\text{SiLi}$  is formed from  $(\text{Ph}_3\text{Ge})_3\text{SiH}$  and Li in  $\text{EtNH}_2$  and is stable in the solid but reacts slowly with the solvent<sup>8</sup>.

The accessibility of hydrosilanes from reduction of commercially available chlorosilanes makes them attractive precursors to silylmetallics. However, the hydridic nature of the Si-H bond may make removal of hydrogen as a proton difficult. Both NaH and KH deprotonate  $\text{Ph}_3\text{SiH}$  as well as  $\text{Et}_3\text{SiH}$  in DME (40°C, 12 h) or HMPA (RT, 6 h) to give<sup>9</sup> quantitative yields of  $\text{R}_3\text{SiK}$  (Na). Addition of  $\text{D}_2\text{O}$  gives  $\text{Ph}_3\text{SiD}$  (85 %) and of  $\text{Me}_3\text{SiCl}$  gives  $\text{Me}_3\text{SiSiEt}_3$  (75 %). This method is effective with both alkyl- and arylsilanes. However, the details of the procedure are not available, and the source and method of cleaning of the metal hydride will be critical to the success of the reaction. Deprotonation of hydrosilanes by methylolithium does not occur, although coupling and elimination of LiH may be observed.

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#### 5.5.4.5. from Tetraorganosilanes with Alkali Metals.

Although  $\text{Ph}_3\text{SiK}$  is formed from reaction of  $\text{Ph}_3\text{SiCPh}_3$ <sup>1</sup> and  $\text{Ph}_3\text{SiCMe}_2\text{Ph}$ <sup>2</sup> with Na-K in  $\text{Et}_2\text{O}$  (70 % and 39 % yield, respectively) this reaction is not an improvement over the methods described earlier (§5.5.4.2, §5.5.4.3 and §5.5.4.4). One application is related to the cleavage<sup>3</sup> of the Si-Ph bonds in  $\text{SiPh}_4$  by Li metal in THF to give  $\text{Ph}_3\text{SiLi}$  (79 %). Although  $\text{Ph}_3\text{SiLi}$  is formed by other routes, selective cleavage of phenyl groups may generate silyllithiums that are otherwise inaccessible, e.g.,  $(\text{Me}_3\text{Si})_2\text{SiPhLi}$  from<sup>4</sup>  $(\text{Me}_3\text{Si})_2\text{SiPh}_2$  and Li metal in tetrahydrofuran (THF). Cleavage of phenyl groups in  $\text{Ph}_2\text{SiH}_2$  in the presence of Li metal contributes<sup>5</sup> to disproportionation of this reagent

5.5. Formation of Bonds between Elements of Groups IVB and IA 185  
 5.5.4. Silicon-Group-IA Bonds

#### 5.5.4.4. from Organosilicon Hydrides with Alkali Metals and Metal Hydrides.

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#### 5.5.4.5. from Tetraorganosilanes with Alkali Metals.

Although  $\text{Ph}_3\text{SiK}$  is formed from reaction of  $\text{Ph}_3\text{SiCPh}_3$ <sup>1</sup> and  $\text{Ph}_3\text{SiCMe}_2\text{Ph}$ <sup>2</sup> with Na-K in  $\text{Et}_2\text{O}$  (70% and 39% yield, respectively) this reaction is not an improvement over the methods described earlier (§5.5.4.2, §5.5.4.3 and §5.5.4.4). One application is related to the cleavage<sup>3</sup> of the Si-Ph bonds in  $\text{SiPh}_4$  by Li metal in THF to give  $\text{Ph}_3\text{SiLi}$  (79%). Although  $\text{Ph}_3\text{SiLi}$  is formed by other routes, selective cleavage of phenyl groups may generate silyllithiums that are otherwise inaccessible, e.g.,  $(\text{Me}_3\text{Si})_2\text{SiPhLi}$  from<sup>4</sup>  $(\text{Me}_3\text{Si})_2\text{SiPh}_2$  and Li metal in tetrahydrofuran (THF). Cleavage of phenyl groups in  $\text{Ph}_2\text{SiH}_2$  in the presence of Li metal contributes<sup>5</sup> to disproportionation of this reagent



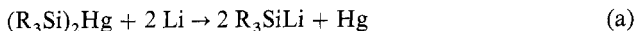
and not formation of a functional silyllithium,  $\text{Ph}_2\text{SiHLi}$ , or to a silyldilithium, such as  $\text{Ph}_2\text{SiLi}_2$ . The Si—Ph bond in  $(\text{c-C}_3\text{H}_5)_3\text{Ph}_3\text{Si}$  is cleaved<sup>6</sup> by a fivefold xs of Li metal in THF (20°C);  $(\text{c-C}_3\text{H}_5)_3\text{Ph}_2\text{SiH}$  in 29 % yield formed on hydrolysis. When  $\text{Ph}_4\text{Si}$  is stirred with Na–K alloy in  $\text{Et}_2\text{O}$  (24 h),  $\text{Ph}_3\text{SiK}$  is formed<sup>7</sup> in 70 % yield (trapping with  $\text{Ph}_3\text{SiCl}$ ).

(J. Y. COREY)

1. A. G. Brook, H. Gilman, L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953).
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7. H. Gilman, T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

#### 5.5.4.6. from Silylmercurials.

Alkylmetallic reagents are the most difficult to generate. Although this problem is now surmounted (see §5.5.4.2.2 and §5.5.4.4), there may still be disadvantages from side products. The alternative route to alkylsilyllithiums of good purity involves a silylmercurial with Li metal:



The method is general, although used primarily for generation of  $\text{Me}_3\text{SiLi}$  and  $\text{Et}_3\text{SiLi}$ . The advantage of the use of silylmercury precursors is that exchange occurs in  $\text{C}_6\text{H}_6$  and organosilyllithiums free of coordinating solvents (ether) may be obtained. In this way  $\text{Me}_3\text{SiLi}$  is prepared and isolated as a pure solid by sublimation<sup>1</sup>.

TABLE 1. ORGANOSILYLMETALLICS FROM SILYLMERCURIALS

Silylmetallic	Starting mercurial (mmol)	Metal (g-at)	Solvent (mL)	T (°C), time (h)	Yield (%)	Method of yield determination <sup>a</sup>	Ref.
$\text{Me}_3\text{SiLi}$	$(\text{Me}_3\text{Si})_2\text{Hg}$ (22)	Li (100)	THF (100)	RT, 3–4	15	$(\text{MeO})_3\text{SiCl}$	3
	$(\text{Me}_3\text{Si})_2\text{Hg}$ (43)	Li (360)	THF (150)	RT, 6	42	$\text{CO}_2$	4
$\text{Et}_3\text{SiLi}$	$(\text{Et}_3\text{Si})_2\text{Hg}$ (20)	Li (140)	THF (20)	RT, 24	<sup>b</sup>	<sup>b</sup>	5
	$\text{Et}_3\text{SiHgEt}$ (92)	Li (210)	$\text{C}_6\text{H}_6$ (25)	RT, 72	80	$\text{Ph}_2\text{SiCl}_2$	5
	$\text{Et}_3\text{SiHgEt}$ (35)	Li (245)	THF (30)	RT, 48	25	$\text{Et}_3\text{SnBr}$	5
	$\text{Et}_3\text{SiHgSSiEt}_3^c$	Li	Hexane	RT, 48	55	$\text{Me}_2\text{SiHCl}$	6
$\text{Et}_3\text{SiNa}$	$(\text{Et}_3\text{Si})_2\text{Hg}$ (5.3)	Na (72)	$\text{C}_6\text{H}_6$ (20)	RT, 144	26	$\text{Et}_3\text{GeBr}^d$	2
$\text{Et}_3\text{SiK}$	$(\text{Et}_3\text{Si})_2\text{Hg}$ (5.7)	K (37)	$\text{C}_6\text{H}_6$ (20)	RT, 144	0	<sup>e</sup>	2
	$(\text{Et}_3\text{Si})_2\text{Hg}$ (6.5)	K (54)	$\text{Et}_3\text{SiH}$ (20)	RT, 120	25	$\text{Me}_2\text{SiCl}^f$	2
$\text{Et}_3\text{Si}_2\text{K}^g$	$\text{Et}_3\text{SiHgSiEt}_3$ (5.3)	K (33)	$\text{C}_6\text{H}_6$ (35)	RT, 144	95	$\text{C}_6\text{H}_6$	2

<sup>a</sup> Reagent indicated was added, and % yield corresponds to coupling product (halosilane) or acid ( $\text{CO}_2$ ) formed.

<sup>b</sup> Not available.

<sup>c</sup> Mixed with  $\text{Et}_3\text{SiLi}$ .

<sup>d</sup> Other products:  $\text{Hg}$  (89%);  $\text{Et}_3\text{SiPh}$  (39%).

<sup>e</sup>  $\text{PhSiEt}_3$  (97%).

<sup>f</sup> Other products formed:  $\text{R}_3\text{SiSiR}_3$  [ $\text{R} = \text{Et}$  (29%),  $\text{Me}$  (42%)].

<sup>g</sup> Mixed with  $\text{Et}_3\text{SiK}$ .

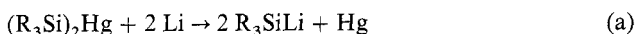
and not formation of a functional silyllithium,  $\text{Ph}_2\text{SiHLi}$ , or to a silyldilithium, such as  $\text{Ph}_2\text{SiLi}_2$ . The Si—Ph bond in  $(\text{c-C}_3\text{H}_5)_3\text{PhSi}$  is cleaved<sup>6</sup> by a fivefold xs of Li metal in THF (20°C);  $(\text{c-C}_3\text{H}_5)_2\text{PhSiH}$  in 29 % yield formed on hydrolysis. When  $\text{Ph}_4\text{Si}$  is stirred with Na—K alloy in  $\text{Et}_2\text{O}$  (24 h),  $\text{Ph}_3\text{SiK}$  is formed<sup>7</sup> in 70 % yield (trapping with  $\text{Ph}_3\text{SiCl}$ ).

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	$(\text{Et}_3\text{Si})_2\text{Hg}$ (6.5)	K (54)	$\text{Et}_3\text{SiH}$ (20)	RT, 120	25	$\text{Me}_2\text{SiCl}^f$	2
$\text{Et}_3\text{Si}_2\text{K}^g$	$\text{Et}_3\text{SiHgSi}_2\text{Et}_5$ (5.3)	K (33)	$\text{C}_6\text{H}_6$ (35)	RT, 144	95	$\text{C}_6\text{H}_6$	2

<sup>a</sup> Reagent indicated was added, and % yield corresponds to coupling product (halosilane) or acid ( $\text{CO}_2$ ) formed.

<sup>b</sup> Not available

<sup>c</sup> Mixed with  $\text{Et}_3\text{SiSLi}$

<sup>d</sup> Other products: Hg (89%);  $\text{Et}_3\text{SiPh}$  (39%).

<sup>e</sup>  $\text{PhSiEt}_3$  (97%).

<sup>f</sup> Other products formed:  $\text{R}_3\text{SiSiR}_3$  [R = Et (29%), Me (42%)].

<sup>g</sup> Mixed with  $\text{Et}_3\text{SiK}$ .

Although useful for preparing silyllithium reagents, the corresponding Na and K reagents, when generated in benzene, react with the solvent to give phenylsilanes<sup>2</sup>.

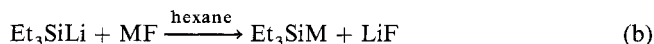
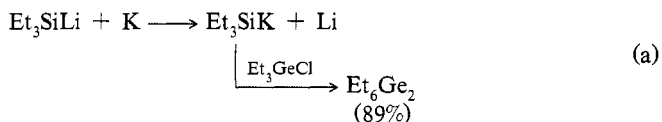
Examples of Eq (a) are given in Table 1.

(J. Y. COREY)

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#### 5.5.4.7. from Exchange.

Silylmetallics of the heavier group-IA elements can be formed from metal exchange with organolithiums. Because condensation of  $R_3SiCl$  ( $R$  = alkyl) with the silylmetallic does not occur in the presence of Rb or Cs (see §5.5.4.3), and the reagent reacts with solvent in the longer time periods required to convert  $(R_3Si)_2Hg$  to  $R_3SiM$  with added Na or K (see §5.5.4.6), exchange is preferred<sup>1,2</sup> for silylrubidium and -cesium reagents:



where M = K (37), Rb (—), Cs (90%). Reaction (b) may be driven by the formation of LiF, which has a high lattice energy. When exchange of  $\text{Et}_3\text{SiLi}$  and KF is performed in  $\text{C}_6\text{H}_6$ , the product is  $\text{Et}_3\text{SiPh}$  (61%)<sup>2</sup>. If KF or CsF is added to  $\text{Et}_3\text{SiLi}$  in hexane, conversion to  $\text{Et}_3\text{SiK}$  and  $\text{Et}_3\text{SiCs}$  occurs<sup>2</sup>.

Halogen-metal exchange occurs between  $\text{Ph}_3\text{SnLi}$  and  $\text{Ph}_3\text{SiCl}$  to generate  $\text{Ph}_3\text{SiLi}$ , which couples with *xs*  $\text{Ph}_3\text{SiCl}$  to give  $\text{Ph}_6\text{Si}_2$ , the product isolated<sup>3</sup>. However, this exchange is not of synthetic utility.

(J Y COREY)

1. D. A. Bravo-Zhivotovskii, I. D. Kalikhman, O. A. Kruglaya, N. S. Vyazankin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 508 (1978).
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3. C. Tamborski, F. E. Ford, E. J. Soloski, *J. Org. Chem.*, 28, 181 (1963).

### 5.5.5. Germanium–Group-IA Bonds

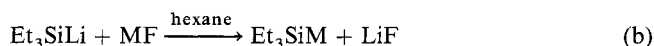
Organogermylmetallics are formed and studied in solution<sup>1,2</sup>. Formation and reactions of germylmetallics are performed under N<sub>2</sub> or Ar in the absence of moisture and O<sub>2</sub>. Solvents must be dried before use. Storage of these reagents is possible, but

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Silylmetallics of the heavier group-IA elements can be formed from metal exchange with organolithiums. Because condensation of  $R_3SiCl$  ( $R = \text{alkyl}$ ) with the silylmetallic does not occur in the presence of Rb or Cs (see §5.5.4.3), and the reagent reacts with solvent in the longer time periods required to convert  $(R_3Si)_2Hg$  to  $R_3SiM$  with added Na or K (see §5.5.4.6), exchange is preferred<sup>1,2</sup> for silylrubidium and -cesium reagents:



Halogen-metal exchange occurs between  $\text{Ph}_3\text{SnLi}$  and  $\text{Ph}_3\text{SiCl}$  to generate  $\text{Ph}_3\text{SiLi}$ , which couples with  $x$   $\text{Ph}_3\text{SiCl}$  to give  $\text{Ph}_6\text{Si}_2$ , the product isolated<sup>3</sup>. However, this exchange is not of synthetic utility.

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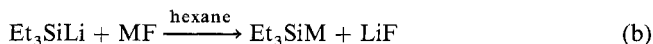
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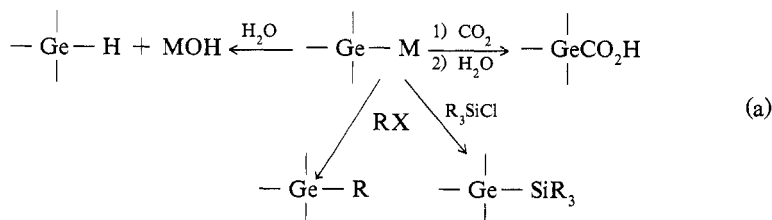
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reaction with solvent occurs with time. Yields are inferred from trapping reactions, which include hydrolysis, coupling with an organic halide or Si(Ge) halide or carbonation:



Solid germymetallics are isolated from  $\text{NH}_3$  ( $\text{KGeH}_3^3$ ,  $\text{Ph}_3\text{GeNa} \cdot 3 \text{NH}_3^4$ ) and from pentane–HMPA (hexamethylphosphoramide) (**a carcinogen**) ( $\text{Et}_3\text{GeLi} \cdot \text{HMPA}$ )<sup>5</sup>.

(J. Y. COREY)

1. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglmya, *Organomet. React.*, 5, 101 (1975).
2. D. D. Davis, C. E. Gray, *Organomet. Chem. Rev.*, A, 6, 283 (1970).
3. G. K. Teal, C. A. Kraus, *J. Am. Chem. Soc.*, 72, 4706 (1950).
4. C. A. Kraus, L. S. Foster, *J. Am. Chem. Soc.*, 49, 457 (1927).
5. O. A. Kruglaya, D. A. Bravo-Zhivotovskii, N. S. Yvazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, 46, 1909 (1976).

### 5.5.5.1. from the Elements.

Among the metal germanides<sup>1</sup>, the Li–Ge phase diagram demonstrates the existence of two compounds,  $\text{Li}_4\text{Ge}_n$  (probably  $\text{Li}_4\text{Ge}$ ) and  $\text{Li}_{3n}\text{Ge}_n$  (probably  $\text{Li}_6\text{Ge}_2$ ). These compounds also are formed by heating the appropriate Li:Ge ratios (4:1 and 3:1, respectively) on crystalline SiC chips as crucibles in a He atmosphere<sup>2</sup>. The reaction of Ge and Na in  $\alpha\text{-Al}_2\text{O}_3$  (corundum) crucibles in hermetically sealed steel bottles at 650–700°C (48 h) under Ar gives<sup>3</sup> NaGe after volatilization of xs Na. The remaining alkali metals react with Ge at 600°C to give MGe ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ )<sup>4</sup>.

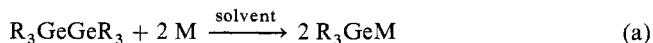
(J. Y. COREY)

1. G. V. Samsonov, V. N. Bondarev, *Germanides*, transl., A. Wold, Primary Sources Publ., New York, 1970.
2. E. Pell, *Phys. Chem. Solids*, 3, 74 (1957).
3. E. Hohnmann, *Z. Anorg. Allg. Chem.*, 257, 113 (1948).
4. R. Schafer, W. Klemm, *Z. Anorg. Allg. Chem.*, 312, 214 (1961).

### 5.5.5.2. from Organodigermanes

#### 5.5.5.2.1. with Alkali Metals.

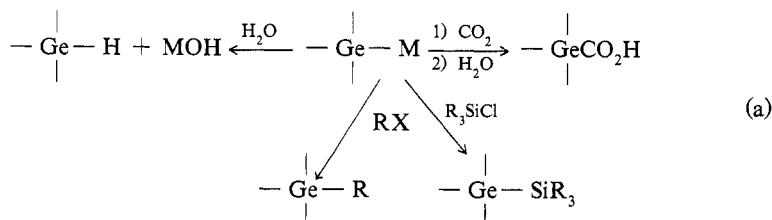
Germymetallics are formed from Ge—Ge-bonded reagents and alkali metals:



The starting digermanes may be formed from  $\text{R}_3\text{GeCl}$  and M (group IA) in  $\text{Et}_2\text{O}$ .

The generation of the germymetallic depends on the solvent. When tetrahydrofuran (THF) is added to  $\text{Ph}_3\text{GeGePh}_3$  and Li metal to form a paste, stirring continued until the

reaction with solvent occurs with time. Yields are inferred from trapping reactions, which include hydrolysis, coupling with an organic halide or Si(Ge) halide or carbonation:



Solid germymetallics are isolated from  $\text{NH}_3$  ( $\text{KGeH}_3$ <sup>3</sup>,  $\text{Ph}_3\text{GeNa} \cdot 3 \text{NH}_3$ <sup>4</sup>) and from pentane-HMPA (hexamethylphosphoramide) (**a carcinogen**) ( $\text{Et}_3\text{GeLi} \cdot \text{HMPA}$ )<sup>5</sup>.

(J. Y. COREY)

1. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglmya, *Organomet. React.*, **5**, 101 (1975).
2. D. D. Davis, C. E. Gray, *Organomet. Chem. Rev.*, **A**, **6**, 283 (1970).
3. G. K. Teal, C. A. Kraus, *J. Am. Chem. Soc.*, **72**, 4706 (1950).
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5. O. A. Kruglaya, D. A. Bravo-Zhivotovskii, N. S. Yvazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **46**, 1909 (1976).

#### 5.5.5.1. from the Elements.

Among the metal germanides<sup>1</sup>, the Li-Ge phase diagram demonstrates the existence of two compounds,  $\text{Li}_n\text{Ge}_n$  (probably  $\text{Li}_4\text{Ge}$ ) and  $\text{Li}_{3n}\text{Ge}_n$  (probably  $\text{Li}_6\text{Ge}_2$ ). These compounds also are formed by heating the appropriate Li:Ge ratios (4:1 and 3:1, respectively) on crystalline SiC chips as crucibles in a He atmosphere<sup>2</sup>. The reaction of Ge and Na in  $\alpha\text{-Al}_2\text{O}_3$  (corundum) crucibles in hermetically sealed steel bottles at 650–700°C (48 h) under Ar gives<sup>3</sup> NaGe after volatilization of xs Na. The remaining alkali metals react with Ge at 600°C to give MGe ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ )<sup>4</sup>.

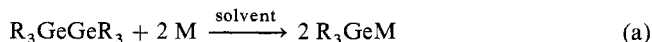
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1. G. V. Samsonov, V. N. Bondarev, *Germanides*, transl., A. Wold, Primary Sources Publ., New York, 1970.
2. E. Pell, *Phys. Chem. Solids*, **3**, 74 (1957).
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4. R. Schafer, W. Klemm, *Z. Anorg. Allg. Chem.*, **312**, 214 (1961).

#### 5.5.5.2. from Organodigermanes

##### 5.5.5.2.1. with Alkali Metals.

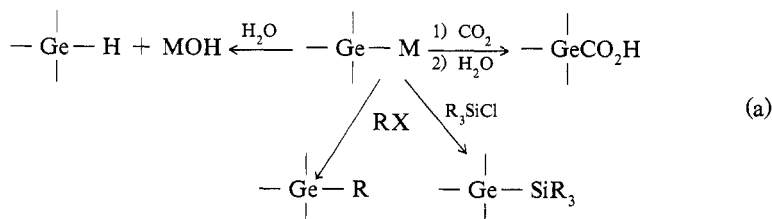
Germymetallics are formed from Ge—Ge-bonded reagents and alkali metals:



The starting digermanes may be formed from  $\text{R}_3\text{GeCl}$  and M (group IA) in  $\text{Et}_2\text{O}$ .

The generation of the germymetallic depends on the solvent. When tetrahydrofuran (THF) is added to  $\text{Ph}_3\text{GeGePh}_3$  and Li metal to form a paste, stirring continued until the

reaction with solvent occurs with time. Yields are inferred from trapping reactions, which include hydrolysis, coupling with an organic halide or Si(Ge) halide or carbonation:



Solid germymetallics are isolated from  $\text{NH}_3$  ( $\text{KGeH}_3$ <sup>3</sup>,  $\text{Ph}_3\text{GeNa} \cdot 3 \text{NH}_3$ <sup>4</sup>) and from pentane-HMPA (hexamethylphosphoramide) (**a carcinogen**) ( $\text{Et}_3\text{GeLi} \cdot \text{HMPA}$ )<sup>5</sup>.

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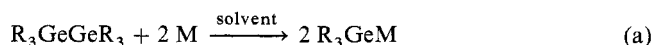
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4. R. Schafer, W. Klemm, *Z. Anorg. Allg. Chem.*, **312**, 214 (1961).

### 5.5.5.2. from Organodigermanes

#### 5.5.5.2.1. with Alkali Metals.

Germymetallics are formed from Ge—Ge-bonded reagents and alkali metals:



The starting digermanes may be formed from  $\text{R}_3\text{GeCl}$  and M (group IA) in  $\text{Et}_2\text{O}$ .

The generation of the germymetallic depends on the solvent. When tetrahydrofuran (THF) is added to  $\text{Ph}_3\text{GeGePh}_3$  and Li metal to form a paste, stirring continued until the



TABLE 1. CLEAVAGE OF GERMANIUM-GERMANIUM BONDS-BY ALKALI METALS, KOEt AND PhLi

Silylmetallic	Starting germane (mmol)	Alkali metal reactant (mmol)	Solvent <sup>a</sup> (mmol)	Time (h), (°C)	Yield (%)	Method of yield determination <sup>b</sup>	Ref.
Ph <sub>3</sub> GeLi	Ph <sub>6</sub> Ge <sub>2</sub> (12)	Li (140)	THF	3, RT	75	PhCH <sub>2</sub> Cl	1
	Ph <sub>6</sub> Ge <sub>2</sub> (10)	Li (140)	DME	5, RT	40	Et <sub>3</sub> SiCl	2
	Ph <sub>6</sub> Ge <sub>2</sub> (15)	Li (140)	THF	120, Δ	11 <sup>c</sup>	H <sub>2</sub> O <sup>d</sup>	3
Ph <sub>3</sub> GeNa	Ph <sub>6</sub> Ge <sub>2</sub>	Na	NH <sub>3</sub>		100		5
	Ph <sub>6</sub> Ge <sub>2</sub> (1.1)	Na (43) <sup>e</sup>	DME (30)	1, RT	100	Me <sub>2</sub> SO <sub>4</sub>	7
Ph <sub>3</sub> GeK	Ph <sub>6</sub> Ge <sub>2</sub> (8.2)	Na-K <sup>f</sup>	Et <sub>2</sub> O	24, RT	88	CO <sub>2</sub>	11
R <sub>3</sub> GeLi <sup>g</sup>	R <sub>6</sub> Ge <sub>2</sub> (60)	Li (130)	HMPA	<0.1, RT	100	H <sub>2</sub> O	9
R <sub>3</sub> GeNa <sup>g</sup>	R <sub>6</sub> Ge <sub>2</sub> (60)	Na (130)	HMPA	<0.1, RT	100	H <sub>2</sub> O	9
R <sub>3</sub> GeK <sup>g</sup>	R <sub>6</sub> Ge <sub>2</sub> (60)	K (130)	HMPA	<0.1, RT	100	H <sub>2</sub> O	9
Et <sub>3</sub> GeK	Et <sub>6</sub> Ge <sub>2</sub>	K	EtNH <sub>2</sub>	9, RT	100	EtBr	8
Ph <sub>2</sub> GeHLi	Ph <sub>2</sub> HGeGeHPh <sub>2</sub> (4)	Li-Hg <sup>h</sup>	THF	30, RT	31	H <sub>2</sub> O	10
Ph <sub>2</sub> GeH <sub>2</sub> Li	PhH <sub>2</sub> GeGeH <sub>2</sub> Ph (21)	Li-Hg <sup>i</sup>	THF	20, RT	44	H <sub>2</sub> O	10
Ph <sub>2</sub> GeNa <sub>2</sub>	(Ph <sub>2</sub> Ge) <sub>4</sub> (1.0)	Na (43) <sup>e</sup>	DME (30)	44, RT	100	Me <sub>2</sub> SO <sub>4</sub>	7

<sup>a</sup> Solvent key: THF, tetrahydrofuran; DME, 1,2-ethyleneglycol dimethyl ether; HMPA, hexamethylphosphoric triamide

<sup>b</sup> Reagent indicated is added and % yield corresponds to coupling product when chlorosilanes or organic halides are added or acid when CO<sub>2</sub> is added.

<sup>c</sup> Also isolated is the solvent cleavage product Ph<sub>3</sub>Ge(CH<sub>2</sub>)<sub>4</sub>OH (23%).

<sup>d</sup> By weight

<sup>e</sup> Naphthalene (3.0 mmol).

<sup>f</sup> 2.5 mL of alloy; THF catalyst.

<sup>g</sup> R = Me, Et, i-Pr, n-Bu.

<sup>h</sup> 6 weeks.

<sup>i</sup> 8 mmol Li in 1 mL Hg.

<sup>j</sup> 43 mmol Li in 3 mL Hg.

paste turns color, and then if more solvent is added, solutions of  $\text{Ph}_3\text{GeLi}$  are formed<sup>1</sup>. Attempts to generate  $\text{Ph}_3\text{GeLi}$  in  $\text{Et}_2\text{O}$  fail, and although 1,2-dimethoxyethane (DME) may be employed, the yields are lower<sup>2</sup>. Prolonged contact of  $\text{Ph}_3\text{GeLi}$  with THF results in decomposition and cleavage of the solvent<sup>3</sup>. The solvent mixture THF-hexamethylphosphoramide (HMPA) is recommended for  $\text{Ar}_3\text{GeLi}$  ( $\text{Ar} = \text{aryl}$ )<sup>4</sup>. Slow reaction of Na metal with  $\text{Ph}_3\text{GeGePh}_3$  occurs in liq  $\text{NH}_3$ , but results vary with size of the Na pieces used and xs Na must be avoided, because  $\text{Ge-Ph}$  bonds are then cleaved<sup>4</sup>. Removal of the solvent gives  $\text{Ph}_3\text{GeNa} \cdot 3 \text{NH}_3$  quantitatively. Solvate-free  $\text{Ph}_3\text{GeNa}$  may be obtained by heating. Cleavage of  $\text{Ph}_6\text{Ge}_2$  by Na metal does not occur in refluxing xylene<sup>2</sup>. With ether alone little or no cleavage of  $\text{Ph}_6\text{Ge}_2$  by Na-K alloy occurs in 24 h, and with THF only reaction of Na-K with solvent occurs, but cleavage occurs with  $\text{Et}_2\text{O}$  as solvent and THF or PhBr added as catalysts<sup>2</sup>. When  $\text{Ph}_6\text{Ge}_2$  and Na-K alloy are heated in  $n\text{-Bu}_2\text{O}$  or xylene (reflux), starting material is consumed but no products are identified<sup>2</sup>. In DME secondary reactions of  $\text{Ph}_3\text{GeK}$  occur with either alloy or solvent, so this solvent cannot be used<sup>2</sup>. Reaction of  $\text{Ph}_6\text{Ge}_2$  with potassium occurs in xylene and DME, but no quenching products of  $\text{Ph}_3\text{GeK}$  are identified<sup>2</sup>. When  $\text{Ph}_6\text{Ge}_2$  and Cs metal are mixed in  $\text{Et}_2\text{O}$  (48 h) only starting material is identified<sup>2</sup> (51%). Lithium cleavage of  $\text{Ph}(\text{i-Pr})_2\text{GeGe}(\text{i-Pr})_2\text{Ph}$  occurs<sup>6</sup> in THF.

Although biphenyl may improve formation of  $\text{R}_3\text{GeM}$  from  $\text{R}_6\text{Ge}_2\text{-M}$ , the radical anion of naphthalene,  $[\text{C}_{10}\text{H}_8]^- \text{Na}^+$ , cleaves<sup>7</sup> the  $\text{Ge-Ge}$  bond of  $\text{Ph}_6\text{Ge}_2$  in DME. This reagent does not cleave  $\text{Ge-C}$  bonds.

Generation of trialkylgermylmetallics from hexaalkyldigermanes and alkali metals is only moderately successful. The digermane,  $(\text{i-Pr})_6\text{Ge}_2$  is unaffected by Li in refluxing DME, but  $\text{Et}_6\text{Ge}_2$  reacts with a potassium-metal film in the solvent  $\text{EtNH}_2$  (6 weeks). Removal of solvent gives  $\text{Et}_3\text{GeK}$  quantitatively<sup>8</sup>. In HMPA quantitative conversion of  $\text{R}_6\text{Ge}_2$  and M (group IA) to  $\text{R}_3\text{GeM}$  ( $\text{M} = \text{Li, Na, K}$ ;  $\text{R} = \text{Me, Et, i-Pr, n-Bu}$ ) occurs<sup>9</sup>. Solutions are stable up to 3 weeks at  $0^\circ\text{C}$ , but removal of solvent at  $50^\circ\text{C}$  causes decomposition.

Germyllithiums in which  $\text{Ge-H}$  bonds are present can be generated. Both  $\text{PhGeH}_2\text{Li}$  and  $\text{Ph}_2\text{GeHLi}$  are formed from the digermane precursor with Li amalgam, but in modest yield<sup>10</sup>. No reaction occurs in  $\text{Et}_2\text{O}$ . The germyl lithium  $(\text{H}_2\text{C}=\text{CH})_3\text{GeLi}$  results<sup>12</sup> from addition of Li metal to  $[(\text{H}_2\text{C}=\text{CH})_3\text{Ge}]_2$ .

Unlike cyclo-polysilanes, which are cleaved by alkali metals to give<sup>7</sup>  $\text{M}(\text{SiR}_2)_n\text{M}$  ( $\text{R} = \text{Ph}$ ),  $(\text{Ph}_2\text{Ge})_4$  with Na in the presence of naphthalene provides<sup>7</sup>  $\text{Ph}_2\text{GeNa}_2$ .

Examples are summarized in Table 1.

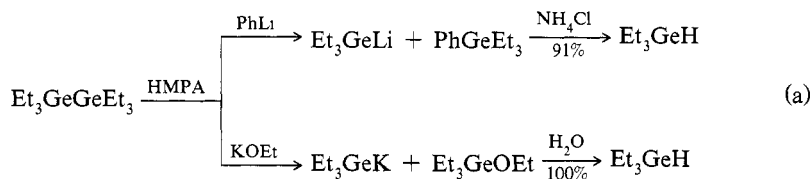
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1. C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, E. J. Soloski, *J. Org. Chem.*, **27**, 619 (1962).
2. H. Gilman, C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5509 (1955).
3. H. Gilman, E. A. Zuech, *J. Org. Chem.*, **26**, 3035 (1961).
4. O. W. Steward, J. E. Dziedzic, J. S. Johnson, *J. Org. Chem.*, **36**, 3475 (1971).
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9. E. J. Bulten, J. G. Noltes, *J. Organomet. Chem.*, **29**, 397 (1971).
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5.5. Formation of Bonds between Elements of Groups IVB and IA 191  
 5.5.5. Germanium–Group-IA Bonds

**5.5.5.2.2. with Alkali-Metal Alkoxides and Organolithiums.**

The Ge—Ge bond is susceptible to nucleophilic attack<sup>1</sup> in hexamethylphosphoramide (HMPA).



The disadvantage of such an approach is that only one-half the Ge in the starting material is converted to product. The cleavage in Eq. (a) does not take place<sup>1</sup> in tetrahydrofuran (THF) at RT or reflux<sup>2</sup>, or in 1,2-dimethoxyethane (DME). When PhLi is added to Ph<sub>6</sub>Ge<sub>2</sub> in Et<sub>2</sub>O, no evidence for the formation of Ph<sub>3</sub>GeLi is obtained<sup>3</sup>.

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**5.5.5.3. from Organohalogermanes with Alkali Metals.**

A more direct route to germymetallic reagents starts from commercially available halogermanes. Because trialkylhalogermanes react with alkali metals in Et<sub>2</sub>O or tetrahydrofuran (THF) (or no solvent) to give<sup>1,2</sup> R<sub>3</sub>Ge<sub>2</sub>, these solvents are not useful for the direct conversion of Ge—Cl to Ge—M. The solvent hexamethylphosphoramide (HMPA) is useful for reacting R<sub>3</sub>GeCl (R = Me, Et, i-Pr, n-Bu) with M (M = Li, Na, K), and 85–90 % conversion to R<sub>3</sub>GeM is claimed but no details are provided<sup>3</sup>. The reaction of Me<sub>3</sub>GeBr and Li in HMPA gives Me<sub>3</sub>GeLi only in low yield<sup>4</sup>. Phenyl substituents on the starting halogermane improve the yield of germyllithium<sup>5</sup>. Attempts to prepare (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeLi from (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeCl and Li metal in THF fail.<sup>7</sup>

TABLE 1. REACTION OF HALOGERMANES WITH ALKALI METALS

Germymetallic	Halogermane (mmol)	M (g-at)	Solvent, time (h)	Yield (%)	Method of determination <sup>a</sup>	Ref.
Ph <sub>3</sub> GeLi	Ph <sub>3</sub> GeCl (16)	Li (80)	THF, 5.5	60	PhCH <sub>2</sub> Cl	6
	Ph <sub>3</sub> GeBr (10)	Li (100)	THF, 3	53	Et <sub>3</sub> SiCl	9
PhMe <sub>2</sub> GeLi	PhMe <sub>2</sub> GeCl (230)	Li (700)	THF <sup>b</sup>	93	PhMe <sub>2</sub> SiCl	5
R <sub>3</sub> GeLi <sup>b</sup>	R <sub>3</sub> GeCl	M <sup>c</sup>	HMPA <sup>d</sup>	85–90	<sup>d</sup>	3
Me <sub>3</sub> SiLi	Me <sub>3</sub> SiBr (60)	Li (240)	HMPA, 12.5	17	CO <sub>2</sub>	4
Bu <sub>2</sub> SiK <sub>2</sub>	Bu <sub>2</sub> SiCl <sub>2</sub> (20)	K (80)	HMPA, 2.5	22	H <sub>2</sub> O	3

<sup>a</sup> Reagent indicated is added and yield corresponds to coupling product when chlorosilanes are added, to germane when H<sub>2</sub>O is added or to acid when CO<sub>2</sub> is added.

<sup>b</sup> Time not specified.

<sup>c</sup> R = Me, Et, i-Pr, n-Bu; M = Li, Na, K.

<sup>d</sup> Details of conditions and method of yield determination not given.

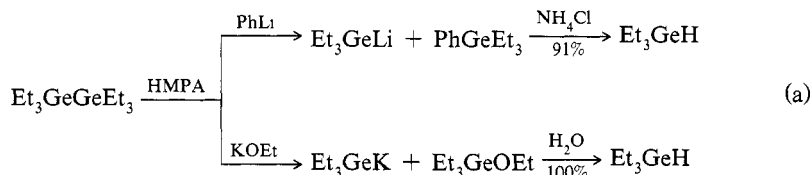
## 5.5. Formation of Bonds between Elements of Groups IVB and IA

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## 5.5.5. Germanium—Group-IA Bonds

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The disadvantage of such an approach is that only one-half the Ge in the starting material is converted to product. The cleavage in Eq. (a) does not take place<sup>1</sup> in tetrahydrofuran (THF) at RT or reflux<sup>2</sup>, or in 1,2-dimethoxyethane (DME). When PhLi is added to Ph<sub>6</sub>Ge<sub>2</sub> in Et<sub>2</sub>O, no evidence for the formation of Ph<sub>3</sub>GeLi is obtained<sup>3</sup>.

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<sup>a</sup> Reagent indicated is added and yield corresponds to coupling product when chlorosilanes are added, to germane when H<sub>2</sub>O is added or to acid when CO<sub>2</sub> is added.

<sup>b</sup> Time not specified

<sup>c</sup> R = Me, Et, i-Pr, n-Bu; M = Li, Na, K

<sup>d</sup> Details of conditions and method of yield determination not given.

Polymetallic derivatives of Ge are rare, but, in contrast to chlorosilane chemistry,  $n\text{-Bu}_2\text{GeCl}_2$  reacts with potassium metal in HMPA to give<sup>3</sup>  $\text{Bu}_2\text{GeK}_2$ . The hot-atom technique is used to generate  $\text{Li}_4\text{Ge}$  from  $\text{GeCl}_4$  and a 100-fold xs of Li vapor. The conversion is low, for 11% of  $\text{GeH}_4$  is formed on hydrolysis, but no digermane is present in the hydrolysis product<sup>8</sup>.

Results are summarized in Table 1.

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Metallation of  $\text{Ph}_3\text{GeH}$  by Na occurs in liq  $\text{NH}_3$ ;  $\text{Ph}_3\text{GeNa}$  is obtained in high yield<sup>8,9</sup>. However, conversion of  $\text{Ar}_3\text{GeH}$  to  $\text{Ar}_3\text{GeLi}$  with Li metal in tetrahydrofuran (THF)–hexamethylphosphoramide (HMPA) occurs in low yield<sup>10</sup>. When Li is added to  $(\text{PhCH}_2)_3\text{GeH}$  in DME both Ge–H and Ge–C bonds are cleaved<sup>11</sup>. Although metallation of trialkylgermane is not known, reaction of  $\text{RGeH}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) with Na in liq  $\text{NH}_3$  gives  $[\text{RGeH}_2]\text{Na}$ . Because more than 1 equiv of  $\text{H}_2$  is evolved, some side reactions also occur<sup>7</sup>. The formation of  $[\text{EtGeH}_2]\text{Li}$  from  $\text{EtGeH}_3$  and Li occurs in  $\text{EtNH}_2$ , and addition of  $i\text{-AmBr}$  gives  $\text{Et}(i\text{-Am})\text{GeH}_2$ , which also reacts<sup>7</sup> with Li in  $\text{EtNH}_2$  to give  $\text{Et}(i\text{-Am})\text{HGeLi}$ .

Deprotonation of  $\text{Ph}_3\text{GeH}$  by  $\text{RLi}$  yields<sup>12</sup>  $\text{Ph}_3\text{GeLi}$ . The reaction in  $\text{Et}_2\text{O}$  is instantaneous; there are no side reactions, and the reagent is generated in high yield and does not react with the solvent<sup>12</sup>. This approach is also used to deprotonate 1,2,3,4,5-pentaphenylgermole<sup>13</sup>, as well as in the generation of optically active germyllithiums<sup>14–16</sup>.

Deprotonation of alkylgermanes and trigermylgermanes is less successful. Several products are obtained<sup>11</sup> from  $(\text{PhCH}_2)_3\text{GeH}$  and  $n\text{-BuLi}$ , and these products arise from Ge–H as well as Ge–C bond cleavage. Although both Ge–C and Ge–H bond cleavages occur on reaction of  $(\text{Ph}_3\text{Ge})_3\text{GeH}$  with  $n\text{-BuLi}$ , reasonable yields of  $(\text{Ph}_3\text{Ge})_3\text{GeLi}$  may be obtained<sup>17</sup>. Deprotonation of trialkylgermanes is unsuccessful<sup>18</sup>.

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Polymetallic derivatives of Ge are rare, but, in contrast to chlorosilane chemistry,  $n\text{-Bu}_2\text{GeCl}_2$  reacts with potassium metal in HMPA to give<sup>3</sup>  $\text{Bu}_2\text{GeK}_2$ . The hot-atom technique is used to generate  $\text{Li}_4\text{Ge}$  from  $\text{GeCl}_4$  and a 100-fold xs of Li vapor. The conversion is low, for 11 % of  $\text{GeH}_4$  is formed on hydrolysis, but no digermane is present in the hydrolysis product<sup>8</sup>.

Results are summarized in Table 1.

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## 5.5.5. Germanium-Group-IA Bonds

## 5.5.5.4. from Organogermanium Hydrides with Alkali Metals and Derivatives.

TABLE 1. REACTION OF ORGANGERMANIUM HYDRIDES WITH ALKALI METALS AND DERIVATIVES

Germylmetallic	GeH (mmol)	M, MH or RLi (mmol)	Solvent, <sup>a</sup> time (h)	Yield (%)	Method of determination <sup>b</sup>	Refs.
Ph <sub>3</sub> GeLi	Ph <sub>3</sub> GeH (20)	n-BuLi (30) PhLi (20)	Et <sub>2</sub> O <sup>c</sup> Et <sub>2</sub> O, 0.08	97	CO <sub>2</sub>	12
		MeLi (20)	Et <sub>2</sub> O, 24 <sup>d</sup>	83	CO <sub>2</sub>	12
Ph <sub>3</sub> GeNa	Ph <sub>3</sub> GeH (20)	NaH (2200)	DME, 4 <sup>e</sup>	77	CO <sub>2</sub>	12
Ph <sub>3</sub> GeK	Ph <sub>3</sub> GeH	Na	NH <sub>3</sub> <sup>f</sup>	70-80	EtI	18
Ar <sub>3</sub> GeLi <sup>h</sup>	Ph <sub>3</sub> GeH (20)	KH (2200)	DME, 1	70	<sup>g</sup>	8,9
	(p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeH	Li (630)	THF-HMPA, 12	35	CO <sub>2</sub>	19
	(m-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> GeH (12.5)	n-BuLi (16)	Hexane-Et <sub>2</sub> O, 0.17 <sup>i</sup>	38	CO <sub>2</sub>	10
R <sub>3</sub> *GeLi	Me(α-Naph)PhGeH	n-BuLi	Et <sub>2</sub> O, 0.5	80	H <sub>2</sub> O	14
	Et(α-Naph)PhGeH (0.33)	n-BuLi (0.4)	Et <sub>2</sub> O <sup>j</sup> , 0.5	26	Ph <sub>3</sub> GeBr	15
n-Bu <sub>3</sub> GeNa	i-Pr(α-Naph)PhGeH (3.1)	n-BuLi (7.2)	Et <sub>2</sub> O, 0.67	70-80	EtI	16
n-Bu <sub>3</sub> GeK	n-Bu <sub>3</sub> GeH	NaH	DME, 4 <sup>e</sup>	70-80	EtI	19
Et(t-Am)GeHLi	Et(t-Am)GeH <sub>2</sub>	KH	DME, 1	87	i-AmBr	7
EtGeH <sub>2</sub> Li	EtGeH <sub>3</sub>	Li	EtNH <sub>2</sub>	64	i-AmBr	7
(Ph <sub>3</sub> Ge) <sub>2</sub> GeLi	(Ph <sub>3</sub> Ge) <sub>2</sub> GeH (4.0)	BuLi (6.0)	Et <sub>2</sub> O, 0.08	54	MeI	17
H <sub>3</sub> GeLi	H <sub>4</sub> Ge (45)	Li	NH <sub>3</sub> <sup>e</sup>	100	<sup>k</sup>	3
H <sub>3</sub> GeNa	H <sub>4</sub> Ge (52)	Na	NH <sub>3</sub> <sup>e</sup>	100	NH <sub>4</sub> Br	7
H <sub>3</sub> GeK	GeH <sub>4</sub>	K	NH <sub>3</sub> <sup>e</sup>	95	MeI	21
	GeH <sub>4</sub>	KNH <sub>2</sub>	HMPA, <0.1 <sup>l</sup>	94		4
H <sub>3</sub> GeRb	GeH <sub>4</sub> (2.76)	K (2.3)	DME, 48			4
H <sub>3</sub> GeCs	GeH <sub>4</sub> (52)	Rb (51)	DME, 48			4
	GeH <sub>4</sub> (52)	Cs (37)	DME, 48			4

<sup>a</sup> Reactions occur at RT unless otherwise specified.<sup>b</sup> Reagent indicated is added, and % yield corresponds to coupling product when organic halide or group-IV halide is added, or to acid when CO<sub>2</sub> is added.<sup>c</sup> Reaction occurs on addition.<sup>d</sup> Reflux.<sup>e</sup> 40°C.<sup>f</sup> -33°C.<sup>g</sup> Cyclohexenone.<sup>h</sup> Ar = p-MeOC<sub>6</sub>H<sub>4</sub>, reagent prepared from 45 mL GeCl<sub>4</sub> and p-MeOC<sub>6</sub>H<sub>4</sub>MgBr followed by treatment with LiAlH<sub>4</sub>.<sup>i</sup> THF-HMPA = 2:1.<sup>j</sup> Ratio hexane-Et<sub>2</sub>O = 1:3.<sup>k</sup> By weight.<sup>l</sup> ca 10°C.

Deprotonation of both  $\text{Ph}_3\text{GeH}$  and  $n\text{-Bu}_3\text{GeH}$  occurs<sup>19</sup> with xs NaH or KH in DME or  $\text{Et}_2\text{O}$ . Deprotonation of  $\text{Ph}_3\text{GeH}$  by  $[\text{CH}_3\text{SOCH}_2]\text{Na}$  in dimethylsulfoxide (DMSO) also occurs, but mixtures of products owing to reaction with the solvent are obtained<sup>20</sup>.

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TABLE 1. CLEAVAGE OF GERMANIUM–CARBON BONDS BY ALKALI METALS

Germane	Alkali	Solvent, T (°C), time (h)	Germyl anion	Yield (%)	Method of yield determination <sup>a</sup>	Refs
Ph <sub>4</sub> Ge	Li	DME, RT, 5–7	Ph <sub>3</sub> GeLi	70	<sup>b</sup>	1
	Na–K	Et <sub>2</sub> O, RT <sup>c</sup>	Ph <sub>3</sub> GeK	40	Ph <sub>3</sub> SiCl	2
Ph <sub>3</sub> GeCPh <sub>3</sub>	Na–K		Ph <sub>3</sub> GeK	26	CO <sub>2</sub>	1
Ph <sub>3</sub> GeCH <sub>2</sub> CH <sub>2</sub> Ph	Li	DME	Ph <sub>3</sub> Ge(CH <sub>2</sub> CH <sub>2</sub> Ph)Li	28.6	n-C <sub>8</sub> H <sub>17</sub> Br <sup>c</sup>	4
(PhCH <sub>2</sub> ) <sub>4</sub> Ge	Li	DME, RT, 1	(PhCH <sub>2</sub> ) <sub>3</sub> GeLi	76	H <sub>2</sub> O	6
		DME, 0, 16	(PhCH <sub>2</sub> ) <sub>3</sub> GeLi	21	H <sub>2</sub> O	
			(PhCH <sub>2</sub> ) <sub>2</sub> GeLi <sub>2</sub>	8	H <sub>2</sub> O <sup>d</sup>	
n-Bu <sub>4</sub> Ge	Li	DME, RT, 96	n-Bu <sub>4</sub> GeLi	0		4
Et <sub>4</sub> Ge	K	HMPA	Et <sub>3</sub> GeK	0	<sup>d</sup>	7

<sup>a</sup> Reagent indicated is added, and % yield corresponds to coupling product when chlorosilanes or organic halides are added to germane when H<sub>2</sub>O is added, or to acid when CO<sub>2</sub> is added.

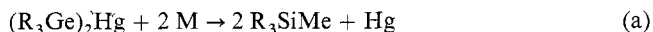
<sup>b</sup> Not specified.

<sup>c</sup> Based on unrecovered starting material

<sup>d</sup> Starting material recovered in 92% yield

#### 5.5.5.6. from Germy–Mercury and –Thallium with Alkali Metals.

Although alkylgermylmetallics may be prepared from R<sub>6</sub>Ge<sub>2</sub> or R<sub>3</sub>GeX (R = alkyl; X = Cl, Br) and M, the solvent required is hexamethylphosphoramide (HMPA). Alternatively digermylmercurials or the corresponding Tl derivatives react with alkali metals:



Alkali metals undergo exchange, and, because the process occurs in hydrocarbon solvent, it is possible to obtain nonsolvated reagents. An apparatus for filling ampules is available<sup>1</sup>. Table 1 gives examples.

(J. Y. COREY)

1. N. S. Vyazankin, E. N. Gladyshev, S. P. Korneva, G. A. Razuvaev, E. A. Arkhangelskaya, *J. Gen. Chem. USSR (Engl. Transl.)*, **38**, 1757 (1968).
2. N. S. Vyazankin, V. T. Bychkov, O. V. Linzina, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, **39**, 940 (1969).
3. D. B. Chambers, F. Glockling, *J. Chem. Soc., A*, 735 (1968).
4. N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, S. P. Korneva, *J. Organomet. Chem.*, **7**, 353 (1967).
5. E. N. Gladyshev, E. A. Fedorova, N. S. Vyazankin, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, **43**, 1306 (1973).
6. E. N. Gladyshev, N. S. Vyazankin, E. A. Fedorova, L. O. Yuntala, G. A. Razuvaev, *J. Organomet. Chem.*, **64**, 307 (1974).
7. E. N. Gladyshev, N. S. Vyazankin, V. S. Andreevichev, A. A. Klimov, G. A. Razuvaev, *J. Organomet. Chem.*, **28**, C42 (1971).
8. G. S. Kalinina, T. A. Basalgiva, N. S. Vyazankin, G. A. Razuvaev, Y. A. Yablokov, N. V. Yablokova, *J. Organomet. Chem.*, **96**, 213 (1975).

5.5. Formation of Bonds between Elements of Groups IVB and IA 195  
 5.5.5. Germanium–Group-IA Bonds

TABLE 1. CLEAVAGE OF GERMANIUM–CARBON BONDS BY ALKALI METALS

Germane	Alkali	Solvent, T (°C), time (h)	Germyl anion	Yield (%)	Method of yield determination <sup>a</sup>	Refs
Ph <sub>4</sub> Ge	Li	DME, RT, 5–7	Ph <sub>3</sub> GeLi	70	<sup>b</sup>	1
	Na–K	Et <sub>2</sub> O, RT <sup>c</sup>	Ph <sub>3</sub> GeK	40	Ph <sub>3</sub> SiCl	2
Ph <sub>3</sub> GeCPh <sub>3</sub>	Na–K		Ph <sub>3</sub> GeK	26	CO <sub>2</sub>	1
Ph <sub>3</sub> GeCH <sub>2</sub> CH <sub>2</sub> Ph	Li	DME	Ph <sub>3</sub> Ge(CH <sub>2</sub> CH <sub>2</sub> Ph)Li	28.6	n-C <sub>8</sub> H <sub>17</sub> Br <sup>c</sup>	4
(PhCH <sub>2</sub> ) <sub>4</sub> Ge	Li	DME, RT, 1	(PhCH <sub>2</sub> ) <sub>3</sub> GeLi	76	H <sub>2</sub> O	6
		DME, 0, 16	(PhCH <sub>2</sub> ) <sub>3</sub> GeLi	21	H <sub>2</sub> O	
			(PhCH <sub>2</sub> ) <sub>2</sub> GeLi <sub>2</sub>	8	H <sub>2</sub> O	
n-Bu <sub>4</sub> Ge	Li	DME, RT, 96	n-Bu <sub>4</sub> GeLi	0	<sup>d</sup>	4
Et <sub>4</sub> Ge	K	HMPA	Et <sub>3</sub> GeK	0	<sup>d</sup>	7

<sup>a</sup> Reagent indicated is added, and % yield corresponds to coupling product when chlorosilanes or organic halides are added to germane when H<sub>2</sub>O is added, or to acid when CO<sub>2</sub> is added.

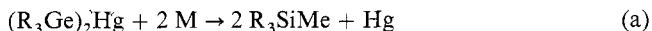
<sup>b</sup> Not specified.

<sup>c</sup> Based on unrecovered starting material

<sup>d</sup> Starting material recovered in 92% yield

5.5.5.6. from Germyl–Mercury and –Thallium with Alkali Metals.

Although alkylgermylmetallics may be prepared from R<sub>6</sub>Ge<sub>2</sub> or R<sub>3</sub>GeX (R = alkyl; X = Cl, Br) and M, the solvent required is hexamethylphosphoramide (HMPA). Alternatively digermylmercurials or the corresponding Tl derivatives react with alkali metals:



Alkali metals undergo exchange, and, because the process occurs in hydrocarbon solvent, it is possible to obtain nonsolvated reagents. An apparatus for filling ampules is available<sup>1</sup>. Table 1 gives examples.

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2. N. S. Vyazankin, V. T. Bychkov, O. V. Linzina, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, **39**, 940 (1969).
3. D. B. Chambers, F. Glockling, *J. Chem. Soc., A*, 735 (1968).
4. N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, S. P. Korneva, *J. Organomet. Chem.*, **7**, 353 (1967).
5. E. N. Gladyshev, E. A. Fedorova, N. S. Vyazankin, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, **43**, 1306 (1973).
6. E. N. Gladyshev, N. S. Vyazankin, E. A. Fedorova, L. O. Yuntala, G. A. Razuvaev, *J. Organomet. Chem.*, **64**, 307 (1974).
7. E. N. Gladyshev, N. S. Vyazankin, V. S. Andreevichev, A. A. Klimov, G. A. Razuvaev, *J. Organomet. Chem.*, **28**, C42 (1971).
8. G. S. Kalinina, T. A. Basalgiva, N. S. Vyazankin, G. A. Razuvaev, Y. A. Yablokov, N. V. Yablokova, *J. Organomet. Chem.*, **96**, 213 (1975).

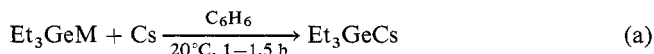
TABLE 1. FORMATION OF GERMANYMETALLICS FROM MERCURY AND THALLIUM DERIVATIVES

Germymetallic	Starting Hg or Tl derivative (mmol)	Metal (g-at)	Solvent (mL)	T (°C) time (h)	Yield (%)	Method of yield determination <sup>a</sup>	Ref.
Ph <sub>3</sub> GeLi	(Ph <sub>3</sub> Ge) <sub>2</sub> Hg (2.9)	Li (100)	THF (10)	20°, 0.2 <sup>b</sup>	66	H <sub>2</sub> O	2
Me <sub>3</sub> GeLi	(Me <sub>3</sub> Ge) <sub>2</sub> Hg	Li	THF				3
Et <sub>3</sub> GeLi	(Et <sub>3</sub> Ge) <sub>2</sub> Hg (7.3)	Li (101)	C <sub>6</sub> H <sub>6</sub> (15)	RT, 24	77	Ph <sub>2</sub> SiCl <sub>2</sub>	4
	(Et <sub>3</sub> Ge) <sub>2</sub> Tl (2.4)	Li (43)	THF	RT, 24	48	Et <sub>3</sub> SiH	4
Et <sub>3</sub> GeNa	(Et <sub>3</sub> Ge) <sub>2</sub> Hg (9.6)	Na (52)	C <sub>6</sub> H <sub>6</sub> (20)		61	Me <sub>3</sub> SiCl	5
Et <sub>3</sub> GeK	(Et <sub>3</sub> Ge) <sub>2</sub> Hg (6.5)	K (23)	C <sub>6</sub> H <sub>6</sub> (25)	RT, 3	69	Me <sub>3</sub> SiCl	5
Et <sub>3</sub> GeRb	(Et <sub>3</sub> Ge) <sub>2</sub> Hg (8.1)	Rb (17)	THF	RT, <0.1	97	Me <sub>3</sub> SiCl	6
Et <sub>3</sub> GeCs	(Et <sub>3</sub> Ge) <sub>2</sub> Hg (8.1)	Cs (17)	C <sub>6</sub> H <sub>6</sub> (20)	RT, <0.1	82-87	Me <sub>3</sub> SiCl	6
i-Pr <sub>3</sub> GeLi	(i-Pr <sub>3</sub> Ge) <sub>2</sub> Hg	Li	C <sub>6</sub> H <sub>6</sub>	40°C, 72	83	<sup>c</sup>	7
(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>3</sub> GeLi	[(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>2</sub> Ge] <sub>2</sub> Hg (4.6)	Li (101)	THF (20)	RT, 8	68	t-BuO <sub>2</sub> But	8

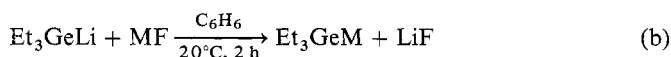
<sup>a</sup> Reagent indicated is added, and % yield corresponds to coupling product when chlorosilanes are added and to germane when CO<sub>2</sub> is added.<sup>b</sup> Not specified.<sup>c</sup> Method of analysis not specified.

### 5.5.5.7. from Exchange and/or Ge(II) Derivatives.

Although little explored, interconversion of  $R_3GeM$  to a derivative of a heavier alkali metal is an alternative route to Rb or Cs derivatives<sup>1</sup>:



where  $M = Li, Na, K$ . A simpler approach<sup>2</sup> is the reaction of  $R_3GeLi$  with metal fluorides (100% mol xs) in  $C_6H_6$ :



where  $M = K, Rb, Cs$ . The course of Eq. (b) can be monitored by NMR.

A route to germyllithiums is reaction of xs  $R_3GeLi$  with a germylene<sup>3</sup>, such as  $GeX_2$  in 1,2-dimethoxyethane (DME), e.g.:



(J. Y. COREY)

1. D. A. Bravo-Zhivotovskii, I. D. Kalikhman, O. A. Kruglaya, N. S. Vyazankin, *Izv. Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 508 (1978).
2. D. A. Bravo-Zhivotovskii, O. A. Kruglaya, I. D. Kalikhman, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, 49, 1464 (1979).
3. F. Glockling, K. A. Hooton, *J. Chem. Soc.*, 1849 (1963).

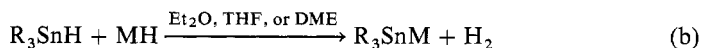
### 5.5.6. Tin-Group-IA Bonds

The methods by which these compounds are prepared are covered in §5.5.4.1-§5.5.4.6, but some additional preparations are noted here.

Specific compounds are obtained by transmetallation of organotin-Cd<sup>1</sup> or organotin-Hg<sup>2</sup> compounds, e.g.:



Cleavage of organotin hydrides by alkali hydrides is used to prepare  $R_3SnNa$  and  $R_3SnK$  compounds<sup>3</sup> with yields >80%:

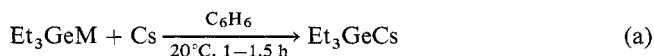


where  $R = Ph$  and  $n-Bu$ ,  $M = Na$  and  $K$  and THF = tetrahydrofuran and DME = 1,2-dimethoxyethane. However, the method fails for  $R_3SnLi$  compounds<sup>3-5</sup>.

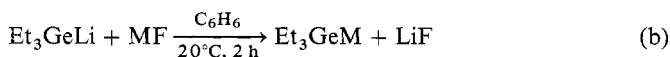
Cleavage of organotin hydrides with organolithiums is not satisfactory. No  $Ph_3SnLi$  is obtained from  $Ph_3SnH$  and  $MeLi$  in ether<sup>6</sup>, and attempts to obtain  $n-Bu_3SnLi$  from  $n-Bu_3SnH$  and  $n-BuLi$  result in low yields when hexamethyl-phosphoramide (HMPA) is used as solvent. The organotin hydride decomposes to hexa-*n*-butylditin before reaction with  $n-BuLi$ <sup>7,8</sup>.

### 5.5.5.7. from Exchange and/or Ge(II) Derivatives.

Although little explored, interconversion of  $R_3GeM$  to a derivative of a heavier alkali metal is an alternative route to Rb or Cs derivatives<sup>1</sup>:



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(J. Y. COREY)

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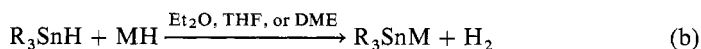
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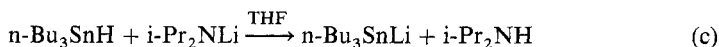
Cleavage of organotin hydrides by alkali hydrides is used to prepare  $R_3SnNa$  and  $R_3SnK$  compounds<sup>3</sup> with yields > 80%:



where  $R = Ph$  and  $n-Bu$ ,  $M = Na$  and  $K$  and THF = tetrahydrofuran and DME = 1,2-dimethoxyethane. However, the method fails for  $R_3SnLi$  compounds<sup>3-5</sup>.

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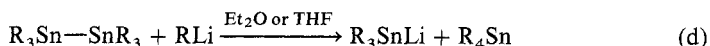
Lithium-hydrogen exchange between  $n\text{-Bu}_3\text{SnH}$  and an aminolithium gives tri- $n$ -butyltin lithium in high yield<sup>9</sup>:



This method is used<sup>10</sup> to obtain  $n\text{-Bu}_3\text{SnK}$  and  $n\text{-Bu}_3\text{SnCs}$ .

Sodium amide cleaves the Sn—Sn bond in hexamethylditin<sup>11</sup>.  $n$ -Dibutylamino-lithium cleaves the Sn—Si bond in  $\text{Me}_3\text{Si—Sn}(\text{Bu-}n)_3$  to give  $\text{Me}_3\text{SiN}(\text{Bu-}n)_2$  in 74% yield. The other product<sup>12</sup> is probably  $n\text{-Bu}_3\text{SnLi}$ .

The Sn—Sn bond in hexaphenylditin is cleaved by phenyllithium<sup>13</sup>, and nearly quantitative yields are obtained on a small (gram) scale<sup>9,14</sup>:



where  $\text{R} = \text{Me}$  or  $n\text{-Bu}$ . For example,  $n\text{-Bu}_3\text{SnLi}$  is prepared by the reaction of hexa- $n$ -butylditin in anhyd THF at  $0^\circ\text{C}$  with  $n\text{-BuLi}$  in hexane. The reaction is complete in 15 min giving a pale-yellow solution ca. 0.34 M in  $n\text{-Bu}_4\text{Sn}$  and  $n\text{-Bu}_3\text{SnLi}$ . The same preparation on a 50-g scale is less satisfactory in  $\text{Et}_2\text{O}$  or THF but gives<sup>8</sup> quantitative yields in HMPA.

Hexaphenylditin is cleaved by  $\text{KH}$  or  $\text{NaH}$  at RT in DME to give  $\text{Ph}_3\text{SnK}$  or  $\text{Ph}_3\text{SnNa}$  in 80% yield<sup>3</sup>.

Preparation of  $(\text{Me}_3\text{Sn})_3\text{SnLi}$  occurs on heating  $\text{Me}_3\text{SnLi}$  in THF for 2 h at  $80^\circ\text{C}$  in the presence of HMPA catalyst<sup>15</sup>.

Reviews<sup>4</sup> and books<sup>16–18</sup> are available.

(A. K. SAWYER)

1. G. S. Kalinina, O. A. Kruglaya, B. I. Petrov, E. A. Shchupak, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **43**, 2215 (1973).
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3. R. J. P. Correu, C. Guerin, private communication, quoted in ref. 4; see also *J. Organomet. Chem.*, **197**, C19 (1980).
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14. W. C. Still, *J. Am. Chem. Soc.*, **99**, 4836 (1977).
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17. M. J. Newlands, in *Organotin Compounds*, A. K. Sawyer, ed., Marcel Dekker, New York, Vol. 3, 1972, p. 881.
18. R. C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, p. 145.

5.5. Formation of Bonds between Elements of Groups IVB and IA  
5.5.6. Tin–Group-IA Bonds

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**5.5.6.1. from the Elements**

More detailed information and references concerning alloys of tin with the alkali metals may be found in refs. 1–4. This section focuses mainly on the intermetallics.

(A. K. SAWYER)

1. J. M. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VII, Longmans Green, New York, 1907, p. 344; and Vol. II, Suppl. II, *The Alkali Metals*, Wiley, New York, 1961; Vol. II, Suppl. III, *The Alkali Metals*, Wiley, New York, 1963.
2. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, 2nd ed., McGraw Hill, New York, 1958.
3. F. A. Shunk, *Constitution of Binary Alloys*, 2nd Suppl., McGraw-Hill, New York, 1969.
4. *Gmelin's Handbuch der Anorganischen Chemie*, Zinn, Teil D, *Legierungen*, Springer-Verlag, Berlin, 1974.

**5.5.6.1.1. Lithium.**

Information on binary intermetallic compounds of Sn and Li is summarized in refs. 1 and 2. The existence of  $\text{Li}_4\text{Sn}$ ,  $\text{Li}_3\text{Sn}_2$  and  $\text{Li}_2\text{Sn}_5$  is indicated<sup>3</sup> by thermal, X-ray<sup>4</sup> and microscopic analysis. Thermal and thermoresistometric analyses yield<sup>5</sup> phase diagrams showing  $\text{LiSn}_2$  ( $\leq 326^\circ\text{C}$ ),  $\text{LiSn}$  (mp  $485^\circ\text{C}$ ),  $\text{Li}_2\text{Sn}$  ( $\leq 502^\circ\text{C}$ ),  $\text{Li}_5\text{Sn}_2$  ( $\leq 720^\circ\text{C}$ ),  $\text{Li}_7\text{Sn}_2$  (mp  $783^\circ\text{C}$ ), and  $\text{Li}_4\text{Sn}$  (mp  $765^\circ\text{C}$ ). The alloys are melted in iron crucibles in an Ar atmosphere. A phase corresponding to  $\text{Li}_{22}\text{Sn}_5$  also exists<sup>6</sup>.

(A. K. SAWYER)

1. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
2. F. A. Shunk, *Constitution of Binary Alloys*, 2nd Suppl., McGraw-Hill, New York, 1969.
3. G. Masing, G. Tammann, *Z. Anorg. Allg. Chem.*, **67**, 183 (1910).
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**5.5.6.1.2. Sodium.**

An alloy of approximate composition  $\text{Na}_2\text{Sn}$  is obtained<sup>1</sup> when tin metal is melted with xs Na and the product heated in a closed crucible, and  $\text{Na}_4\text{Sn}$  is obtained<sup>2</sup> from Na in liq  $\text{NH}_3$  with Sn metal or tin salts, along with another compound<sup>3</sup> with a higher % Sn. The unstable  $\text{Na}_4\text{Sn}$  is obtained in the reduction of Sn salts by Na amalgam<sup>4</sup>. A salt-like compound,  $\text{Na}_4\text{Sn}_9$ , stable only in  $\text{NH}_3$ , is obtained<sup>5</sup> on treating an Na–Sn alloy with liq  $\text{NH}_3$ . Upon extraction of xs Na from melted Sn and Na with liq  $\text{NH}_3$ , crystals of  $\text{Na}_{15}\text{Sn}_4$ , which may be the same as  $\text{Na}_4\text{Sn}$ , are obtained<sup>6</sup>. Thermal analysis detects<sup>7</sup>  $\text{Na}_4\text{Sn}$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{Na}_4\text{Sn}_3$ ,  $\text{NaSn}$  and  $\text{NaSn}_2$ , the last three believed to undergo polymorphic transformations. From the cooling curves taken in glass tubes in an  $\text{N}_2$  atmosphere, the phase diagram indicates<sup>8</sup> nine compounds:  $\text{Na}_4\text{Sn}$  (mp  $408^\circ\text{C}$ ),  $\text{Na}_3\text{Sn}$ ,  $\text{Na}_2\text{Sn}$  (mp  $487^\circ\text{C}$ ),  $\text{Na}_4\text{Sn}_3$  (mp  $479^\circ\text{C}$ ),  $\text{NaSn}$  (mp  $578^\circ\text{C}$ ),  $\text{NaSn}_2$ ,  $\text{NaSn}_3$ ,  $\text{NaSn}_4$  and  $\text{NaSn}_6$ . All are metallic and decompose on melting except where the mp is given. Electromotive force (emf) measurements at RT show breaks<sup>9–11</sup> at  $\text{Na}_4\text{Sn}$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{NaSn}$  and  $\text{NaSn}_2$ , but not for  $\text{Na}_4\text{Sn}_3$ .

(A. K. SAWYER)



## 5.5. Formation of Bonds between Elements of Groups IVB and IA

### 5.5.6. Tin-Group-IA Bonds

199

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More detailed information and references concerning alloys of tin with the alkali metals may be found in refs. 1-4. This section focuses mainly on the intermetallics.

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##### 5.5.6.1.2. Sodium.

An alloy of approximate composition  $\text{Na}_2\text{Sn}$  is obtained<sup>1</sup> when tin metal is melted with xs Na and the product heated in a closed crucible, and  $\text{Na}_4\text{Sn}$  is obtained<sup>2</sup> from Na in liq  $\text{NH}_3$  with Sn metal or tin salts, along with another compound<sup>3</sup> with a higher % Sn. The unstable  $\text{Na}_4\text{Sn}$  is obtained in the reduction of Sn salts by Na amalgam<sup>4</sup>. A salt-like compound,  $\text{Na}_4\text{Sn}_9$ , stable only in  $\text{NH}_3$ , is obtained<sup>5</sup> on treating an Na-Sn alloy with liq  $\text{NH}_3$ . Upon extraction of xs Na from melted Sn and Na with liq  $\text{NH}_3$ , crystals of  $\text{Na}_{15}\text{Sn}_4$ , which may be the same as  $\text{Na}_4\text{Sn}$ , are obtained<sup>6</sup>. Thermal analysis detects<sup>7</sup>  $\text{Na}_4\text{Sn}$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{Na}_4\text{Sn}_3$ ,  $\text{NaSn}$  and  $\text{NaSn}_2$ , the last three believed to undergo polymorphic transformations. From the cooling curves taken in glass tubes in an  $\text{N}_2$  atmosphere, the phase diagram indicates<sup>8</sup> nine compounds:  $\text{Na}_4\text{Sn}$  (mp  $408^\circ\text{C}$ ),  $\text{Na}_3\text{Sn}$ ,  $\text{Na}_2\text{Sn}$  (mp  $487^\circ\text{C}$ ),  $\text{Na}_4\text{Sn}_3$  (mp  $479^\circ\text{C}$ ),  $\text{NaSn}$  (mp  $578^\circ\text{C}$ ),  $\text{NaSn}_2$ ,  $\text{NaSn}_3$ ,  $\text{NaSn}_4$  and  $\text{NaSn}_6$ . All are metallic and decompose on melting except where the mp is given. Electromotive force (emf) measurements at RT show breaks<sup>9-11</sup> at  $\text{Na}_4\text{Sn}$ ,  $\text{Na}_2\text{Sn}$ ,  $\text{NaSn}$  and  $\text{NaSn}_2$ , but not for  $\text{Na}_4\text{Sn}_3$ .

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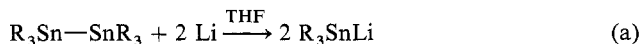
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#### 5.5.6.2.1. Lithium.

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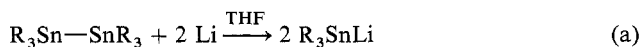
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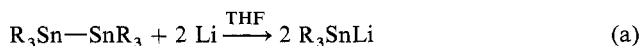
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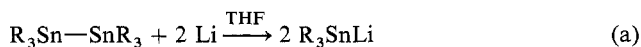
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#### 5.5.6.1.5. Cesium.

A 1 : 1 intermetallic, CsSn, is obtained in high vacuum or an Ar atmosphere; it has a tetragonal (NaPb-type) structure<sup>1</sup>.

(A. K. SAWYER)

1. I. F. Hewaidy, E. Bushman, W. Klemm, *Z. Anorg. Allg. Chem.*, 328, 283 (1964).

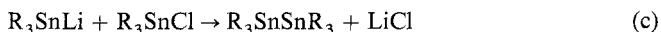
### 5.5.6.2. from Organodistannanes with Alkali Metals

#### 5.5.6.2.1. Lithium.

Trialkyl- and triphenyltin lithium are prepared by reacting<sup>1,2</sup> metallic Li with hexaalkylditins or hexaphenylditin, respectively, in tetrahydrofuran (THF):



where R = Me, n-Bu or Ph. This method has advantages over previous methods, using either an alkyllithium compound and tin(II) chloride, or trialkyltin chloride and Li metal. The latter mechanism<sup>1</sup> involves formation of the hexaalkylditin followed by its reaction with Li metal:



where R = CH<sub>3</sub> or n-C<sub>4</sub>H<sub>9</sub>.

A similar mechanism obtains for triphenyltin lithium<sup>2</sup>. Alkyllithiums and tin(II) chloride leads to the product<sup>3</sup>:



where R = C<sub>2</sub>H<sub>5</sub> or n-C<sub>4</sub>H<sub>9</sub>. However, n-Bu<sub>3</sub>SnLi prepared in this way reacts<sup>4</sup> with Me<sub>3</sub>SiCl to give none of the expected Me<sub>3</sub>SiSn(Bu-n)<sub>3</sub>, but instead, n-BuSiMe<sub>3</sub> and n-Bu<sub>4</sub>Sn; the n-Bu<sub>3</sub>SnLi acts as if it were a mixture of n-Bu<sub>2</sub>Sn and n-BuLi. By contrast, the organotin lithium obtained by Eq. (a) gives the expected product with Me<sub>3</sub>SiCl in 78% yield:



The organotin lithium compounds are prepared by stirring a mixture of the hexaorganoditin with xs Li metal in THF. On reaction, which often requires heating, a change in color occurs to an olive-green-black mixture which gives<sup>5</sup> a positive Color Test I. After filtering through glass, the filtrate containing the organotin lithium is used for subsequent experiments<sup>1,8</sup>. Color Test I indicates the presence of M—Li bonds<sup>5</sup>.

Triphenyltin lithium is prepared by the action of Li metal on hexaphenylditin<sup>2,6-8</sup>. Triphenyltin lithium prepared in different ways often gives different results in reactions. Preparations from either triphenyltin chloride or hexaphenylditin with Li metal in THF are the most satisfactory, yielding the expected products. Of these two methods, the preparation from the organoditin is preferred owing to higher purity of the starting material and higher yields obtained.

The triphenyltin lithium reagent is dark olive-green and is stable to refluxing in THF for at least 24 h with no solvent cleavage. Samples of Ph<sub>3</sub>SnLi in THF stored at 0°C for over 1 month show no sign of decomposition as measured by titration. The Ph<sub>3</sub>SnLi reagent gives a positive Color Test I which may be used to follow the reactions. The lack of benzoic acid formation on carbonation of the reagent immediately after its formation or after 24 h of refluxing, indicates that triphenyltin lithium does not exist in equilibrium with diphenyltin and phenyllithium<sup>8</sup>.

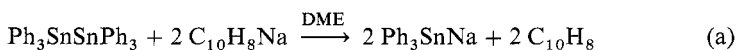
Titration of ca. 0.5 M Li in liq NH<sub>3</sub> (–70°C) with 0.5 M hexaalkylditin in THF gives >95% yields. This method is more economical but less convenient than treatment of hexaalkylditins with alkyllithiums<sup>9</sup>.



1. C. Tamborski, F. E. Ford, E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963).
2. C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, E. J. Soloski, *J. Org. Chem.*, **27**, 619 (1962).
3. H. Gilman, S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 2507 (1953).
4. D. Blake, G. E. Coates, J. M. Tate, *J. Chem. Soc.*, 618 (1961).
5. H. Gilman, F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1952).
6. R. K. Ingham, S. D. Rosenberg, H. Gilman, *Chem. Rev.*, **60**, 513 (1960).
7. H. Gilman, O. L. Marrs, S. Sim, *J. Org. Chem.*, **27**, 4232 (1962).
8. C. Tamborski, F. E. Ford, E. J. Soloski, *J. Org. Chem.*, **28**, 181 (1963).
9. W. C. Still, *J. Am. Chem. Soc.*, **99**, 4836 (1977).

### 5.5.6.2.2. Sodium.

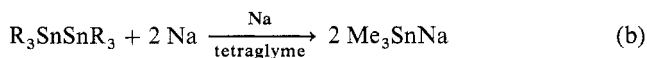
Organotin sodium compounds are prepared by the action of Na naphthalene on organoditins, in 1,2-dimethoxyethane (DME) in 75 % yield<sup>1</sup>:



The preparation involves addition of Na naphthalene in DME at 0°C to a stirred suspension of hexaphenylditin in the same solvent in a 2 : 1 Na–hexaphenylditin ratio. The dark-green color of the Na naphthalene is rapidly discharged, and the reaction mixture turns deep violet when half of the Na naphthalene is added. At the equivalence point the color fades to the pale tan of triphenyltin sodium. The solution remaining is used for further reactions.

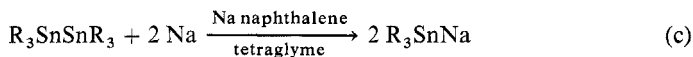
Compounds  $\text{R}_3\text{SnNa}$  and  $\text{R}_2\text{SnNa}_2$  where  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$ ,  $n\text{-C}_4\text{H}_9$ ,  $s\text{-C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$  and  $\text{cyclo-C}_6\text{H}_{11}$  are formed<sup>2</sup> for use in making organotin deuterides, which are used in turn to obtain C-deuterated compounds in high yields.

Trimethyltin sodium, prepared by cleavage of hexamethylditin with either Na metal or Na naphthalene in tetraglyme is used in mechanistic studies of organotin alkalis with organic halides<sup>3–7</sup>:



The preparation is carried out under  $\text{N}_2$  in 85–90 % yields<sup>5</sup>. The clear yellow-green trimethyltin sodium solution is stable for days when stored under a dry, inert atmosphere<sup>3</sup>.

The cleavage of hexaalkylditins by Na naphthalene is used to prepare trimethyl-, triethyl-, tri-*n*-butyl- and trivinyltin sodium<sup>7</sup>:



where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $n\text{-Bu}$  or vinyl.

(A. K. SAWYER)

1. D. Blake, G. E. Coates, J. M. Tate, *J. Chem. Soc.*, 618 (1961).
2. K. Kulheim, W. P. Neumann, H. Mohring, *Angew. Chem., Int. Ed. Engl.*, **7**, 455 (1968).
3. H. G. Kuivila, K. R. Wursthorn, *J. Organomet. Chem.*, **105**, C6 (1976).
4. H. G. Kuivila, F. V. DiStefano, *J. Organomet. Chem.*, **122**, 171 (1976).
5. K. R. Wursthorn, H. G. Kuivila, *J. Organomet. Chem.*, **140**, 29 (1977).
6. H. G. Kuivila, K. R. Wursthorn, *Tetrahedron Lett.*, 4357 (1975).
7. K. R. Wursthorn, H. G. Kuivila, G. F. Smith, *J. Am. Chem. Soc.*, **100**, 2779 (1978).

## 202 5.5. Formation of Bonds between Elements of Groups IVB and IA

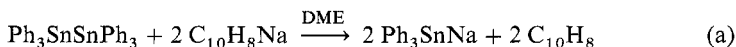
## 5.5.6. Tin-Group-IA Bonds

## 5.5.6.2. from Organodistannanes with Alkali Metals

1. C. Tamborski, F. E. Ford, E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963).
2. C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, E. J. Soloski, *J. Org. Chem.*, **27**, 619 (1962).
3. H. Gilman, S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 2507 (1953).
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7. H. Gilman, O. L. Marrs, S. Sim, *J. Org. Chem.*, **27**, 4232 (1962).
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## 5.5.6.2.2. Sodium.

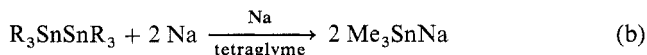
Organotin sodium compounds are prepared by the action of Na naphthalene on organodistins, in 1,2-dimethoxyethane (DME) in 75% yield<sup>1</sup>:



The preparation involves addition of Na naphthalene in DME at 0°C to a stirred suspension of hexaphenylditin in the same solvent in a 2:1 Na-hexaphenylditin ratio. The dark-green color of the Na naphthalene is rapidly discharged, and the reaction mixture turns deep violet when half of the Na naphthalene is added. At the equivalence point the color fades to the pale tan of triphenyltin sodium. The solution remaining is used for further reactions.

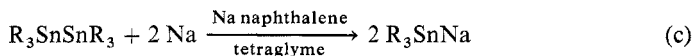
Compounds  $\text{R}_3\text{SnNa}$  and  $\text{R}_2\text{SnNa}_2$  where  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$ ,  $n\text{-C}_4\text{H}_9$ ,  $s\text{-C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$  and  $\text{cyclo-C}_6\text{H}_{11}$  are formed<sup>2</sup> for use in making organotin deuterides, which are used in turn to obtain C-deuterated compounds in high yields.

Trimethyltin sodium, prepared by cleavage of hexamethylditin with either Na metal or Na naphthalene in tetraglyme is used in mechanistic studies of organotin alkalis with organic halides<sup>3-7</sup>:



The preparation is carried out under  $\text{N}_2$  in 85-90% yields<sup>5</sup>. The clear yellow-green trimethyltin sodium solution is stable for days when stored under a dry, inert atmosphere<sup>3</sup>.

The cleavage of hexaalkylditins by Na naphthalene is used to prepare trimethyl-, triethyl-, tri-*n*-butyl- and trivinyltin sodium<sup>7</sup>:



where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $n\text{-Bu}$  or vinyl.

(A. K. SAWYER)

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7. K. R. Wursthorn, H. G. Kuivila, G. F. Smith, *J. Am. Chem. Soc.*, **100**, 2779 (1978).

5.5. Formation of Bonds between Elements of Groups IVB and IA 203  
 5.5.6. Tin-Group-IA Bonds

**5.5.6.2.3. Potassium.**

Hexamethyldigermane resists cleavage by an Na-K alloy in 1,2-dimethoxyethane (DME) (in which the hexamethyl compounds are soluble), but the Sn-Sn bond is cleaved by the same alloy, yielding trimethyltin potassium<sup>1</sup>:



Solutions of the Na-K alloy in DME are made by melting the metals together in vacuo and distilling on ether which is freshly dried over  $\text{LiAlH}_4$ . Immediate reaction occurs at RT on contact with hexamethylditin in a sealed tube under vacuum to give a greenish-yellow solution. Within 10 min the tube is opened under  $\text{N}_2$  and the solution filtered into tri-p-tolylbromostannane in a 2:1 ratio for identification. 1,1,1-Trimethyl-2,2,2-tri-p-tolyldistannane is obtained in 38% yield.

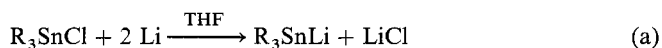
(A. K. SAWYER)

1. M. P. Brown, G. W. A. Fowles, *J. Chem. Soc.* 2811 (1958).

**5.5.6.3. from Organotin Halides with Alkali Metals**

**5.5.6.3.1. Lithium.**

Triphenyltin lithium is synthesized<sup>1-4</sup> from organotin halides with xs Li metal in tetrahydrofuran (THF):

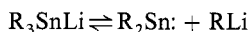


Similarly,  $\text{Me}_3\text{SnLi}$ <sup>5</sup>,  $\text{Et}_3\text{SnLi}$ <sup>6</sup>,  $n\text{-Bu}_3\text{SnLi}$ <sup>5</sup>,  $n\text{-Pr}_3\text{SnLi}$ <sup>7</sup>,  $\text{MePh}_2\text{SnLi}$ <sup>8</sup>,  $(\text{PhCH}_2)_3\text{SnLi}$ <sup>9</sup> and  $\text{Me}(\text{Ph})\text{CHCH}_2(\text{Me})(\text{R})\text{SnLi}$  (where  $\text{R} = \text{Me}$  or  $\text{Ph}$ ) are prepared<sup>10</sup>. Likewise, a dithiotin compound,  $\text{Ph}_2\text{SnLi}_2$ , is prepared<sup>11</sup>.

Titration of ca. 0.5 M Li in liq  $\text{NH}_3$  ( $-70^\circ\text{C}$ ) with ca. 0.5 M trialkyltin halides in THF is used to give trialkyltin lithiums in 70-80% yield<sup>12</sup>.

Lithium naphthalene is used with  $\text{Me}_3\text{SnCl}$  to give  $\text{Me}_3\text{SnLi}$  in ethers, including THF, 1,2-dimethoxyethane (DME), THF-tetraglyme,  $\text{Et}_2\text{O-THF}$ , and tetrahydropyran<sup>13</sup> (THP).

Pentaalkylditin lithium,  $\text{R}_5\text{Sn}_2\text{Li}$  ( $\text{R} = \text{Me}$ ,  $n\text{-Pr}$ ,  $i\text{-Pr}$ ) is present in preparations of  $\text{R}_3\text{SnLi}$  reagents prepared from the trialkyltin halide and Li metal in THF. The  $\text{R}_5\text{Sn}_2\text{Li}$  species arise by oxidative addition of  $\text{R}_3\text{SnLi}$  to the stannylene  $\text{R}_2\text{Sn}$ : which in turn is a significant component of the equilibrium:



Evidence for the presence of these species is obtained<sup>14</sup> by  $^{119}\text{Sn}$  NMR and alkylation to the corresponding  $\text{R}_5\text{Sn}_2\text{R}'$  compounds where  $\text{R}' = \text{Me}$  and cyclo- $\text{C}_6\text{H}_{11}$ .

(A. K. SAWYER)

1. R. K. Ingham, S. D. Rosenberg, H. Gilman, *Chem. Rev.*, **60**, 459 (1960).
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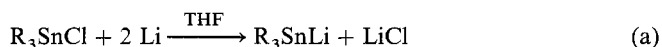
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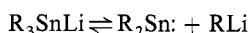


Similarly,  $\text{Me}_3\text{SnLi}$ <sup>5</sup>,  $\text{Et}_3\text{SnLi}$ <sup>6</sup>,  $n\text{-Bu}_3\text{SnLi}$ <sup>5</sup>,  $n\text{-Pr}_3\text{SnLi}$ <sup>7</sup>,  $\text{MePh}_2\text{SnLi}$ <sup>8</sup>,  $(\text{PhCH}_2)_3\text{SnLi}$ <sup>9</sup> and  $\text{Me}(\text{Ph})\text{CHCH}_2(\text{Me})(\text{R})\text{SnLi}$  (where R = Me or Ph) are prepared<sup>10</sup>. Likewise, a dilithiotin compound,  $\text{Ph}_2\text{SnLi}_2$ , is prepared<sup>11</sup>.

Titration of ca. 0.5 M Li in liq  $\text{NH}_3$  ( $-70^\circ\text{C}$ ) with ca. 0.5 M trialkyltin halides in THF is used to give trialkyltin lithiums in 70–80% yield<sup>12</sup>.

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Pentaalkylditin lithium,  $\text{R}_5\text{Sn}_2\text{Li}$  (R = Me, *n*-Pr, *i*-Pr) is present in preparations of  $\text{R}_3\text{SnLi}$  reagents prepared from the trialkyltin halide and Li metal in THF. The  $\text{R}_5\text{Sn}_2\text{Li}$  species arise by oxidative addition of  $\text{R}_3\text{SnLi}$  to the stannylene  $\text{R}_2\text{Sn}$ : which in turn is a significant component of the equilibrium:



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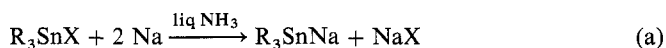
(A. K. SAWYER)

1. R. K. Ingham, S. D. Rosenberg, H. Gilman, *Chem. Rev.*, **60**, 459 (1960).
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3. C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, E. J. Soloski, *J. Org. Chem.*, **27**, 619 (1962).
4. C. Tamborski, F. E. Ford, E. J. Soloski, *J. Org. Chem.*, **28**, 181 (1963).

5. C. Tamborski, F. E. Ford, E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963).
6. W. P. Newmann, R. Sommer, *Justus Liebigs Ann. Chem.*, **701**, 28 (1967).
7. E. C. Juenge, T. E. Snider, Y. E. Lee, *J. Organomet. Chem.*, **22**, 403 (1970).
8. H. Gilman, F. K. Cartledge, S. Y. Sims, *J. Organomet. Chem.*, **4**, 332 (1965).
9. K. Jacob, E. Panse, K. H. Thiele, *Z. Anorg. Allg. Chem.*, **425**, 151 (1976).
10. Y. Tondeur, Ph.D. Thesis, Free Univ. of Brussels (1979).
11. H. Schumann, K. F. Thom, M. Schmidt, *J. Organomet. Chem.*, **2**, 97 (1964).
12. W. C. Still, *J. Am. Chem. Soc.*, **99**, 4836 (1977).
13. H. G. Kuivila, J. L. Considine, R. H. Sherma, R. J. Mynott, *J. Organomet. Chem.*, **111**, 179 (1976).
14. W. Kitching, H. A. Olsگوی, G. M. Drew, *Organometallics*, **1**, 1244 (1982).

### 5.5.6.3.2. Sodium.

Organotin sodiums are obtained from organotin halides with Na in liq NH<sub>3</sub>:



where R = Me, Et, Ph; X = Cl, Br. Using this method Me<sub>3</sub>SnNa<sup>1-2</sup>, Et<sub>3</sub>SnNa<sup>3</sup>, and Ph<sub>3</sub>SnNa<sup>4-5</sup> are obtained. Because of the reactivity of the solvent, preparations use ethers. Because the first step of the reaction of the organotin halides with Na metal is the formation of the hexaorganoditin, which is then followed by cleavage of the ditins by Na metal to give the triorganotin sodium, improved procedures start directly with the hexaorganoditins (see §5.5.4.2).

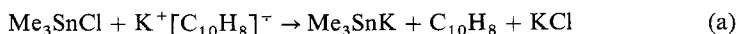
Triphenyltin sodium is prepared from triphenyltin bromide with sodium naphthalene in either<sup>5</sup> tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), and Me<sub>3</sub>SnNa is prepared<sup>6</sup> in ethers using Me<sub>3</sub>SnCl with Na naphthalene in THF, DME and THF-tetraglyme. Trimethyltin sodium is also prepared<sup>7</sup> by adding Me<sub>3</sub>SnBr dropwise with a heated pipet to Na in liq NH<sub>3</sub> at -78°C under Ar.

(A. K. SAWYER)

1. C. A. Kraus, W. N. Greer, *J. Am. Chem. Soc.*, **44**, 2629 (1922).
2. C. A. Kraus, W. V. Sessions, *J. Am. Chem. Soc.*, **47**, 2361 (1925).
3. V. S. Tavgorodini, A. A. Petrov, *Dokl. Akad. Nauk. SSSR*, **143**, 855 (1962).
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5. D. Blake, G. E. Coates, J. M. Tate, *J. Chem. Soc.*, 618 (1961).
6. H. G. Kuivila, J. L. Considine, J. D. Kennedy, *J. Am. Chem. Soc.*, **94**, 7206 (1972).
7. C. H. W. Jones, P. Parington, R. M. G. Roberts, *J. Organomet. Chem.*, **32**, 201 (1971).

### 5.5.6.3.3. Potassium.

Following the method first reported for the preparation of triphenyltin sodium using Na naphthalene<sup>1</sup>, trimethyltin potassium is prepared by the action of trimethyltin chloride on potassium naphthalene in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), or THF-tetraglyme mixture<sup>2</sup>:



Solutions of the reagent are then used for further reactions.

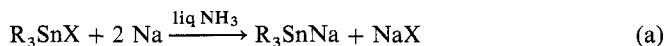
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### 5.5.6.3.2. Sodium.

Organotin sodiums are obtained from organotin halides with Na in liq NH<sub>3</sub>:



where R = Me, Et, Ph; X = Cl, Br. Using this method Me<sub>3</sub>SnNa<sup>1-2</sup>, Et<sub>3</sub>SnNa<sup>3</sup>, and Ph<sub>3</sub>SnNa<sup>4-5</sup> are obtained. Because of the reactivity of the solvent, preparations use ethers. Because the first step of the reaction of the organotin halides with Na metal is the formation of the hexaorganoditin, which is then followed by cleavage of the ditins by Na metal to give the triorganotin sodium, improved procedures start directly with the hexaorganoditins (see §5.5.4.2).

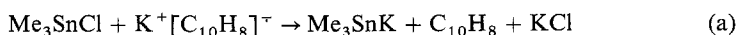
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### 5.5.6.3.3. Potassium.

Following the method first reported for the preparation of triphenyltin sodium using Na naphthalene<sup>1</sup>, trimethyltin potassium is prepared by the action of trimethyltin chloride on potassium naphthalene in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), or THF-tetraglyme mixture<sup>2</sup>:



Solutions of the reagent are then used for further reactions.

(A. K. SAWYER)

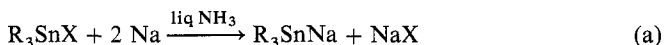
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204      5.5. Formation of Bonds between Elements of Groups IVB and IA  
 5.5.6. Tin-Group-IA Bonds  
 5.5.6.3. from Organotin Halides with Alkali Metals

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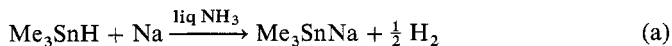
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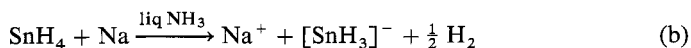
5.5. Formation of Bonds between Elements of Groups IVB and IA 205  
 5.5.6. Tin-Group-IA Bonds

**5.5.6.4. from Organotin Hydrides with Alkali Metals.**

Salt-like trimethyltin sodium is obtained from<sup>1</sup> trimethyltin hydride with Na in liq NH<sub>3</sub>:

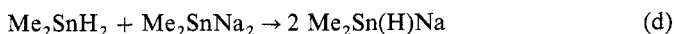
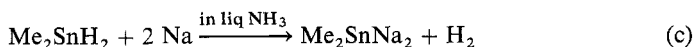


Conductivity and H<sub>2</sub> evolution monitoring of Na in liq NH<sub>3</sub> treated with stannane (SnH<sub>4</sub>) give<sup>2</sup> NaSnH<sub>3</sub> and Na<sub>2</sub>SnH<sub>2</sub>. The former decomposes at -63.5°C in the absence of NH<sub>3</sub>, whereas the latter is more stable, decomposing at >0°C. Nuclear magnetic resonance studies confirm Na[SnH<sub>3</sub>] in solution:



Addition of MeCl to stannane with xs Na in liq NH<sub>3</sub> gives both Me<sub>2</sub>SnH<sub>2</sub> and MeSnH<sub>3</sub>, which suggests the presence of both Na<sub>2</sub>SnH<sub>2</sub> and NaSnH<sub>3</sub>. However, no resonance is found that can be attributed to the [SnH<sub>2</sub>]<sup>2-</sup> ion<sup>3</sup>.

Conductometric titrations of dimethyltin dihydride with Na Metal give evidence for the formation of dimethyltin disodium and dimethyltin hydride sodium<sup>4</sup>:



Dimethyltin hydride sodium (which is not prepared pure) decomposes at 20°C to give sym-tetramethylditin disodium.

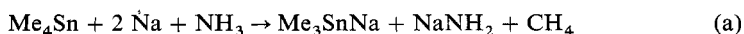
The organotin ions derived from [Me<sub>2</sub>SnH]Na and [MeSnH<sub>2</sub>]Na are obtained<sup>3</sup> from the corresponding organotin hydrides using Na in liq NH<sub>3</sub>, and [Ph<sub>2</sub>SnH]Na, [PhSnH<sub>2</sub>]Na and [(PhCH<sub>2</sub>)<sub>2</sub>SnH]Na are obtained similarly. No evidence is found for [Ph<sub>2</sub>Sn]<sup>2-</sup> 2 Na<sup>+</sup>; however, NMR evidence for Ph<sub>2</sub>SnH<sub>2</sub> with Na in liq NH<sub>3</sub> indicates the formation of sym-tetraphenylditin disodium.

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**5.5.6.5. from Tetraorganotins with Alkali Metals.**

Tetramethyltin reacts with Na in liq NH<sub>3</sub> to yield trimethyltin sodium<sup>1</sup>:

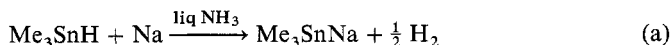


when Me<sub>4</sub>Sn is added dropwise to stirred Na in a 2 : 1 ratio in liq NH<sub>3</sub> under Ar and with exclusion of moisture and CO<sub>2</sub>. After the Me<sub>4</sub>Sn is added the original blue color of the solution changes to pale yellow with a white precipitate. Addition of 1-bromoadamantane in petroleum ether gives the expected adamantyltrimethyltin compound in 65% yield<sup>2</sup>.

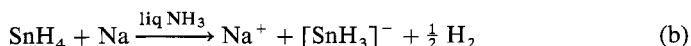


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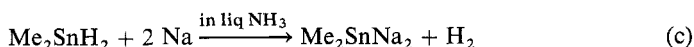


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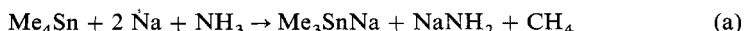
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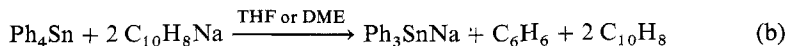
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Triphenyltin sodium is obtained by reaction of Na naphthalene with tetraphenyltin in tetrahydrofuran (THF) or in 1,2-dimethoxyethane (DME):



Phenylsodium is formed in the first step in 65% yield and subsequently reacts with the solvent. Conversion of the  $\text{Ph}_3\text{SnNa}$  by  $\text{EtBr}$  gives  $\text{Ph}_3\text{SnEt}$ . Yields of  $\text{Ph}_3\text{SnNa}$  under similar conditions using Na naphthalene and hexaphenylditin or triphenyltin bromide are 75 and 60%, respectively<sup>3</sup>.

1,1-Dimethyl-1-stannacyclopentane reacts with Li metal in THF to give a complex mixture containing, in addition to polymer, both endocyclic and exocyclic C—Sn bonds<sup>4</sup>.

The mechanisms of the reactions of crotyltrimethyltin<sup>5</sup> or propenyltrimethyltin<sup>6</sup> with Li metal involve cleavage of the crotyl and propenyl groups, respectively, with the concurrent formation of  $\text{Me}_3\text{SnLi}$ .

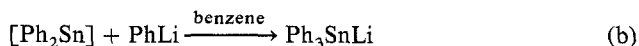
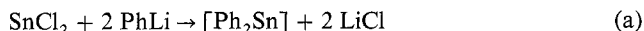
Cleavage of the Sn—C bond in bis(trimethylstannyl)methane occurs<sup>7</sup> using Na in liq  $\text{NH}_3$  with the formation of trimethyltin sodium and  $\text{CH}_4$ .

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#### 5.5.6.6. from Tin(II) Compounds with Organoalkali Reagents.

In an old process, triphenyltin lithium is obtained by reaction of phenyllithium in ether with diphenyltin in benzene<sup>1,2</sup>:

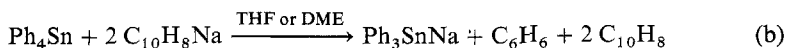


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In a manner analogous to that for triphenyltin lithium, tri-p-tolytin lithium is prepared from p-tolyl lithium and anhyd tin(II) chloride in  $\text{Et}_2\text{O}$  at  $-10^\circ\text{C}$  under  $\text{N}_2$ . Tri-m-tolyltin lithium and tri-o-tolyltin lithium are obtained similarly<sup>4</sup>.

Trialkyltin lithium compounds are prepared<sup>5</sup> following the same procedure as for triphenyltin lithium<sup>3</sup>. Tri-n-butyltin lithium and triethyltin lithium are prepared by

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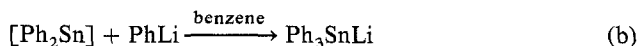
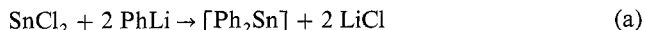
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Trialkyltin lithium compounds are prepared<sup>5</sup> following the same procedure as for triphenyltin lithium<sup>3</sup>, Tri-n-butyltin lithium and triethyltin lithium are prepared by

adding *n*-BuLi or EtLi, respectively, in ether to a suspension of finely ground, anhyd tin(II) chloride suspended in Et<sub>2</sub>O at  $-10^{\circ}\text{C}$ .

Trimethyltin lithium is prepared<sup>6</sup> by the direct reaction of MeLi with anhyd tin(II) chloride in tetrahydrofuran (THF) at  $-78^{\circ}\text{C}$ . Attempts to isolate Me<sub>3</sub>SnLi as a pure substance fail. Although it is stable in THF, attempts to remove solvent even at  $-78^{\circ}\text{C}$  leads to the formation of (Me<sub>3</sub>Sn)<sub>3</sub>SnLi·3 THF along with Me<sub>4</sub>Sn and an insoluble methyltinlithium solid.

The preparation of (Ph<sub>3</sub>Sn)<sub>4</sub>Sn involves the intermediate formation of (Ph<sub>3</sub>Sn)<sub>3</sub>SnLi by reaction of Ph<sub>3</sub>SnLi in THF to SnCl<sub>2</sub> in THF at  $0^{\circ}\text{C}$  in a 3 : 1 ratio. Reaction of this solution with 1 mol of Ph<sub>3</sub>SnCl in THF yields the desired (Ph<sub>3</sub>Sn)<sub>4</sub>Sn in 55% yield<sup>7</sup>.

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## 5.5.7. Lead-Group-IA Bonds

### 5.5.7.1. in Alloys and Intermetallics

Alloys and intermetallics of Pb and the alkali metals except Fr, find interest, especially the Pb-Na system for the industrial synthesis of alkyllead antiknock compounds. The Pb-Li system, e.g., the Li<sub>17</sub>Pb<sub>83</sub> eutectic may be used as a liquid breeder in the thermonuclear fission reactor<sup>1-3</sup>. The tendency for compound formation with the alkali metals decreases from Li to Cs<sup>4</sup>.

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The Pb-Li alloys are produced by fusing proper amounts in an Fe crucible in a quartz tube under inert atmosphere<sup>1,2</sup>; e.g., Li-Pb is prepared by heating the metals to ca.

5.5. Formation of Bonds between Elements of Groups IVB and IA 207

adding *n*-BuLi or EtLi, respectively, in ether to a suspension of finely ground, anhyd tin(II) chloride suspended in Et<sub>2</sub>O at -10°C.

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The following examples illustrate methods for alloys and intermetallics.

The Pb-Li alloys are produced by fusing proper amounts in an Fe crucible in a quartz tube under inert atmosphere<sup>1,2</sup>; e.g., Li-Pb is prepared by heating the metals to ca.

750° and then, for 3 h, to 550°C. On cooling, Li-Pb crystallizes<sup>2</sup> at 483°C. The Li-Pb also separates from melts<sup>3</sup> containing 17–50% Li. Analogously,  $\text{Li}_8\text{Pb}_3$  (previously<sup>3</sup>  $\text{Li}_5\text{Pb}_2$ )<sup>4</sup>,  $\text{Li}_3\text{Pb}$ ,  $\text{Li}_7\text{Pb}_2$  and  $\text{Li}_{22}\text{Pb}_5$  (previously<sup>3</sup>  $\text{Li}_4\text{Pb}$ )<sup>5</sup> are obtained from melts containing 62–70, 70.0–72.1, 72.1–77.8 and 83.0–99.0% Li, respectively<sup>3</sup>. Also,  $\text{Li}_{22}\text{Pb}_5$  is formed<sup>5,6</sup> by a peritectic reaction between  $\text{Li}_7\text{Pb}_2$  and the melt at ca. 650°C.

The Pb-Na alloys with high Na content (71–89 at % Na = 21–47 wt% Na) are made on a laboratory scale in a steel bomb in an electric furnace at 420°C by fusing the components<sup>7</sup>, and Pb-Na alloys with lower Na content are prepared by adding Na metal lumps to molten Pb at the lowest possible T using a steel crucible<sup>8,9</sup>. Fireclay crucibles are also used<sup>10</sup>.

Procedures for Pb-Na alloys suitable for synthesizing the tetramethyl- and tetraethyllead antiknock compounds on a large scale are based on the same principles as the laboratory methods but are adapted to handling large amounts<sup>11</sup> and to obtaining material with proper surface area, gross structure of the alloy, etc.<sup>12</sup>.

Lead-sodium compounds, such as  $\text{Na}_{15}\text{Pb}$ ,<sup>13</sup>  $\text{Na}_9\text{Pb}_4$ <sup>14</sup> or  $\text{NaPb}$ <sup>15</sup>, are prepared from the melt.

The high reactivity of metallic K, Rb and Cs demands special precautions. In laboratory preparation<sup>16</sup> of K-Pb alloys potassium is introduced into molten Pb in Fe crucibles under an inert atmosphere.

The compounds  $\text{KPb}$ <sup>16</sup> and  $\text{KPb}_2$ <sup>17</sup> are obtained by melting stoichiometric amounts of K and Pb metals under inert gas in Fe crucibles, whereas  $\text{RbPb}$  and  $\text{CsPb}$ , which are isomorphous with  $\text{KPb}$ , are prepared in a Ta<sup>18</sup> or  $\alpha\text{-Al}_2\text{O}_3$  (corundum) crucible in Ar in a closed steel bomb<sup>19,20</sup>. Addition of Pb metal powder to molten alkali metals and annealing for one week at 300°C yields<sup>21</sup>  $\text{KPb}$ ,  $\text{RbPb}$  or  $\text{CsPb}$ .

Alloys and intermetallic compounds with more than two components are prepared by fusion as are the binary mixtures<sup>22</sup>; e.g., Pb-K-Na alloys are prepared<sup>23</sup> by mixing a molten Na-K alloy with Pb metal.

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1. A. Zalkin, W. J. Ramsey, *J. Phys. Chem.*, **61**, 1413 (1957).
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#### 5.5.7.1.2. by Reduction.

Reaction of 100 parts finely divided Pb and 11 parts NaH at 300°C is described as a method for the production of active Pb-Na alloys having the composition NaPb for tetraethyllead manufacture. Alloys containing 18.2–30.7 wt % Na can also be made when the NaH ratio is increased<sup>1</sup>.

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Alloys of Pb and alkali metals can be produced by electrolysis from H<sub>2</sub>O or from melts of alkali metal salts at Pb electrodes.

Using a Pb amalgam, cathode production of Pb-alkali-metal alloys from aq alkalichloride is possible. The electrolysis is performed at ca. 40°–80°C. The Pb-alkali-metal alloy is separated from the amalgam on cooling. Residual Hg is evaporated<sup>1</sup>. Formation of Li-Pb compounds during electrolysis of LiOH solns at a Pb cathode is inferred from measurements<sup>2</sup>.

Electrolysis of an NaOH-Na<sub>2</sub>CO<sub>3</sub> melt in a cell using an Ni anode and a molten Pb cathode at 350°–370°C gives Pb-Na alloys with various Na concentrations depending on conditions<sup>3</sup>. Also Na<sub>2</sub>SO<sub>4</sub><sup>4</sup>, NaF or NaCl<sup>5,6</sup> or Na<sub>2</sub>S<sup>6</sup> are employed as melts using different types of fluxes, e.g., cryolite.

Electrolysis of melts of potassium salts yields Pb alloys of varying potassium content when T and type of potassium salt are changed. From a KCl-K<sub>2</sub>CO<sub>3</sub> melt, alloys with 11.8–14.6 wt % K are produced at 675°–730°C<sup>7</sup>; from a KCl-KF melt at 680°C, alloys with 6–7 wt % K separate<sup>7</sup>. From a KOH-NaOH melt, Pb-K alloys with ca. 3 wt % K are gained at 400°C; subsequent melting with KOH at 420°C decreases the Na content of these alloys, while the potassium content is increased<sup>8</sup>. Analogously, alloys with more than two components can be made; e.g., Pb-K-Na alloys separate from a melt of NaCl-KCl-Na<sub>2</sub>CO<sub>3</sub> at 650°–750°C at a molten Pb cathode<sup>9,10</sup> and Pb-Ca-K alloys are obtained<sup>11</sup> by electrolysis of a melt of CaCl<sub>2</sub> and KCl at a liq Pb cathode at 800°C.

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5.5. Formation of Bonds between Elements of Groups IVB and IA 209  
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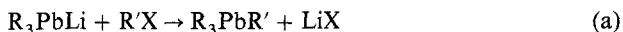
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1. H. N. Gilbert, Ger. Pat. 714,456 (1939); C. 1942, I, 1556; *Chem. Abstr.*, **38**, 1692 (1944).
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### 5.5.7.2. from Hexaorganodiplumbanes

Organolead-alkali compounds are the least stable of the group-IVB-alkali compounds. They are thermolabile and air and moisture sensitive but are stabilized in such donor solvents as Et<sub>2</sub>O, tetrahydrofuran (THF) or NH<sub>3</sub>. Information on their isolation is sparse and no physical properties of pure R<sub>3</sub>PbM (M = alkali metal) or R<sub>2</sub>PbM<sub>2</sub> are available. Nevertheless, R<sub>3</sub>PbM in situ is a powerful tool for synthesizing unsymmetrical R<sub>3</sub>PbR' tetraorganoleads:



The compositions R<sub>3</sub>PbM are deduced by conversion to benzyltriorganoleads on addition of benzylchloride to R<sub>3</sub>PbM solns<sup>1-3</sup>. They are complexes<sup>4-6</sup> of a diorgano-lead(II) compound with an organoalkali metal derivative, analogous to alkali haloplumbates(II).

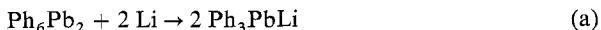
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#### 5.5.7.2.1. with Alkali Metals.

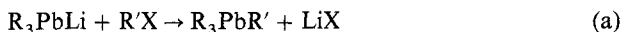
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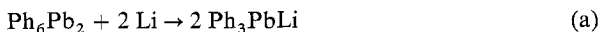
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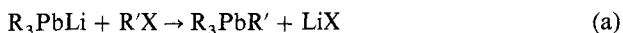
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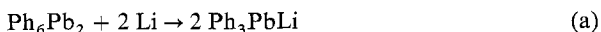
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#### 5.5.7.2.1. with Alkali Metals.

Solutions of Ph<sub>3</sub>PbLi are prepared from Ph<sub>6</sub>Pb<sub>2</sub> and Li metal in tetrahydrofuran (THF)<sup>1,2</sup>:



No Pb—C bonds of the organolead starting compound are lost, as they are in other preparations (see §5.5.7.3). Low T prevents side reactions. Excess Li metal insures that all  $\text{Ph}_6\text{Pb}_2$  is cleaved<sup>3</sup>; however, a large xs of Li metal must be avoided because it reacts with  $\text{Ph}_3\text{PbLi}$  and Pb metal precipitates<sup>4,5</sup>. For example, to 0.1 mol of  $\text{Ph}_6\text{Pb}_2$  in THF (250 mL), 0.214 mol of Li shavings are added and the mixture is stirred for 1 day at  $-20^\circ\text{C}$  under  $\text{N}_2$ . The resulting mixture is filtered under  $\text{N}_2$  into a storage bottle and the filtrate made up with THF to 300 mL. The color of the reaction mixture varies from green to brown immediately after reaction. After standing for several days, a dark-brown sludge settles, leaving a clear-yellow soln of  $\text{Ph}_3\text{PbLi}$  in THF<sup>1,4,5</sup> which can be kept in the absence of air for months<sup>6</sup>. Similarly, tricyclohexylplumbyllithium is obtained<sup>7</sup>. Tri-*p*-tolylplumbyllithium is prepared<sup>6</sup> by stirring (*p*-tolyl)<sub>6</sub>Pb<sub>2</sub> with Li metal in THF at  $20^\circ\text{C}$  for 2–3 days in ca. 45% yield.

Reaction of  $\text{Ph}_6\text{Pb}_2$  and Li metal can also be accomplished<sup>1</sup> in liq  $\text{NH}_3$ , or at RT in 1,2-dimethoxyethane (DME) for 7 days<sup>9</sup>.

Solutions of  $\text{Ph}_3\text{PbNa}$  are obtained analogously from<sup>10–13</sup>  $\text{Ph}_6\text{Pb}_2$  and Na metal in THF, or <sup>2,14–16</sup> in liq  $\text{NH}_3$ . The reaction in THF requires finely divided Na metal. The reaction is slower<sup>12,13</sup> than with Li metal.

A lemon-yellow solid crystallizes from a saturated solution of  $\text{Ph}_6\text{Pb}_2$  and Na metal in  $\text{NH}_3$  when the  $\text{NH}_3$  is evaporated under reduced pressure and below  $-34^\circ\text{C}$ . The solid, for which no analytical data are available<sup>14</sup>, becomes cream colored when  $\text{NH}_3$  is removed completely.

Solutions of tris(*p*-tolyl)-, tris(*p*-ethoxyphenyl)-, tris(*o*-methoxyphenyl)- and tris(cyclohexyl)lead sodium in  $\text{NH}_3$  can be prepared<sup>2,17</sup> in the same way as those of  $\text{Ph}_3\text{PbNa}$ . Tricyclohexyllead sodium is also obtained when hexacyclohexyldilead and Na metal are reacted in  $\text{Et}_2\text{O}$ <sup>18</sup>.

Hexaphenyldilead also reacts with potassium and Rb in liq  $\text{NH}_3$  to give  $\text{Ph}_3\text{PbK}$  and  $\text{Ph}_3\text{PbRb}$  solns, respectively<sup>15</sup>.

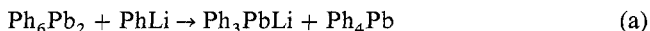
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212      5.5. Formation of Bonds between Elements of Groups IVB and IA  
 5.5.7. Lead-Group-IA Bonds

**5.5.7.2.2. with Organoalkali Reagents.**

Triphenyllead lithium is formed<sup>1-4</sup> in Et<sub>2</sub>O or tetrahydrofuran (THF) at RT along with Ph<sub>4</sub>Pb from Ph<sub>6</sub>Pb<sub>2</sub> and PhLi:



This reaction offers no synthetic advantage, because the reactions of Ph<sub>6</sub>Pb<sub>2</sub> and Li metal (§5.5.7.2.1), of Ph<sub>3</sub>PbCl and Li metal (§5.5.7.4) or of PbCl<sub>2</sub> and PhLi (§5.5.7.5) are less complicated by formation of by-products<sup>2</sup>.

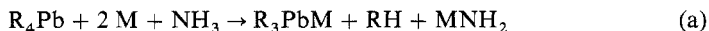
Because Ph<sub>6</sub>Pb<sub>2</sub> is formed during synthesis of Ph<sub>4</sub>Pb from PbCl<sub>2</sub> and PhLi, in discussing the mechanism of this reaction (see §5.2.10.3), Eq. (a) has to be considered.

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**5.5.7.3. from Tetraorganoleads with Alkali Metals.**

Lead-group-IA element bonds are formed by reacting tetraorganoleads with alkali metals, mainly Na, in liq NH<sub>3</sub> or NH<sub>3</sub>-Et<sub>2</sub>O mixtures:



where M = alkali metal.

The reactivity of the alkali metals with R<sub>4</sub>Pb, e.g., in the reaction with Ph<sub>4</sub>Pb, decreases K, Na > Li. Lithium and Na metals are about equally reactive<sup>1,2</sup> with Et<sub>4</sub>Pb.

Trimethyllead lithium can be prepared according to Eq. (a) (M = Li) in liq NH<sub>3</sub> at -78°C in a sealed tube<sup>3</sup>. The solvent is important; (vinyl)<sub>4</sub>Pb with Li metal in Et<sub>2</sub>O forms vinylolithium and not the triorganolead lithium<sup>4</sup>.

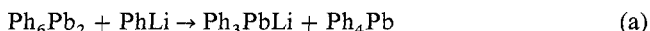
Triorganolead sodium compounds, e.g., Et<sub>3</sub>PbNa<sup>2,5</sup>, vinyl<sub>3</sub>PbNa<sup>6</sup> or Ph<sub>3</sub>PbNa<sup>2</sup>, are obtained from tetraorganoleads with Na metal according to Eq. (a) (M = Na) in Et<sub>2</sub>O-NH<sub>3</sub>. This solvent mixture is better than NH<sub>3</sub> alone<sup>2</sup>. Ether alone is unsatisfactory. Nevertheless, tricyclohexyllead sodium can be prepared by shaking a slurry of finely divided Na metal with hexacyclohexyldilead in ether<sup>7</sup>. However, reaction of Et<sub>4</sub>Pb and Na or Na-K alloy in Et<sub>2</sub>O in the absence of NH<sub>3</sub> gives ethylsodium, but no Pb-Na bounds<sup>8</sup>.

The ease of cleaving of Pb-C bonds by Na in liq NH<sub>3</sub> is ordered: allyl > benzyl ≈ s-butyl > n-butyl > ethyl > methyl > phenyl > p-dimethylaminophenyl, consistent with a mechanism involving nucleophilic attack of Na at the carbon atom having the lowest electron density<sup>9</sup>.

Information on the possibility of preparing compounds of the type R<sub>2</sub>R'PbNa is sparse. The reaction of Et<sub>3</sub>PbPh with Na in liq NH<sub>3</sub> gives Et<sub>2</sub>PhPbNa; however, attempts to prepare unsymmetrical compounds with R' = benzyl or allyl fail<sup>1</sup>.

**5.5.7.2.2. with Organoalkali Reagents.**

Triphenyllead lithium is formed<sup>1-4</sup> in Et<sub>2</sub>O or tetrahydrofuran (THF) at RT along with Ph<sub>4</sub>Pb from Ph<sub>6</sub>Pb<sub>2</sub> and PhLi:



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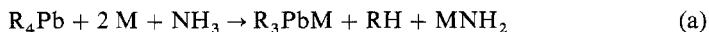
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where M = alkali metal.

The reactivity of the alkali metals with R<sub>4</sub>Pb, e.g., in the reaction with Ph<sub>4</sub>Pb, decreases K, Na > Li. Lithium and Na metals are about equally reactive<sup>1,2</sup> with Et<sub>4</sub>Pb.

Trimethyllead lithium can be prepared according to Eq. (a) (M = Li) in liq NH<sub>3</sub> at -78°C in a sealed tube<sup>3</sup>. The solvent is important; (vinyl)<sub>4</sub>Pb with Li metal in Et<sub>2</sub>O forms vinyl lithium and not the triorganolead lithium<sup>4</sup>.

Triorganolead sodium compounds, e.g., Et<sub>3</sub>PbNa<sup>2,5</sup>, vinyl<sub>3</sub>PbNa<sup>6</sup> or Ph<sub>3</sub>PbNa<sup>2</sup>, are obtained from tetraorganoleads with Na metal according to Eq. (a) (M = Na) in Et<sub>2</sub>O-NH<sub>3</sub>. This solvent mixture is better than NH<sub>3</sub> alone<sup>2</sup>. Ether alone is unsatisfactory. Nevertheless, tricyclohexyllead sodium can be prepared by shaking a slurry of finely divided Na metal with hexacyclohexyldilead in ether<sup>7</sup>. However, reaction of Et<sub>4</sub>Pb and Na or Na-K alloy in Et<sub>2</sub>O in the absence of NH<sub>3</sub> gives ethylsodium, but no Pb-Na bounds<sup>8</sup>.

The ease of cleaving of Pb-C bonds by Na in liq NH<sub>3</sub> is ordered: allyl > benzyl ≈ s-butyl > n-butyl > ethyl > methyl > phenyl > p-dimethylaminophenyl, consistent with a mechanism involving nucleophilic attack of Na at the carbon atom having the lowest electron density<sup>9</sup>.

Information on the possibility of preparing compounds of the type R<sub>2</sub>R'/PbNa is sparse. The reaction of Et<sub>3</sub>PbPh with Na in liq NH<sub>3</sub> gives Et<sub>2</sub>PhPbNa; however, attempts to prepare unsymmetrical compounds with R' = benzyl or allyl fail<sup>1</sup>.



The preparation of organolead sodium compounds is reviewed<sup>10</sup>.

Trimethyllead potassium is prepared<sup>3</sup> by reacting  $\text{Me}_4\text{Pb}$  and potassium in liq  $\text{NH}_3$ .

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Triorganolead alkali compounds can be prepared from  $\text{R}_3\text{PbX}$  (X = halide) with alkali metals in polar solvents, such as tetrahydrofuran (THF) or liq  $\text{NH}_3$ :



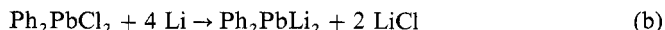
(where M = Li, Na), although the methods described in §5.5.7.2 and §5.5.7.3 are preferred.

On stirring  $\text{Me}_3\text{PbBr}$  with xs freshly cut Li metal in THF at  $-78^\circ\text{C}$  for 2 h, a green solution is formed<sup>1</sup>, the behavior of which is consistent with its containing  $\text{Me}_3\text{PbLi}$ ;  $\text{Et}_3\text{PbLi}$  is prepared analogously<sup>2</sup>. The reaction of  $\text{Ph}_3\text{PbCl}^{3-6}$  or (p-tolyl) $_3\text{PbCl}^6$  with Li metal carried out at  $-20^\circ\text{C}$ . Excess Li metal must be avoided, because it may react further with  $\text{Ph}_3\text{PbLi}$  to give Pb metal<sup>3-6</sup>. Proper control of T is essential. In the preparation<sup>7</sup> of (p-tolyl) $_3\text{PbLi}$ , the mixture is first stirred for 1.5 h at  $-20^\circ\text{C}$ , then for 2 h at RT; the yield is ca. 70%.

The reaction of  $\text{Ph}_3\text{PbCl}$  with Li metal according to Eq. (a) proceeds via intermediate formation of  $\text{Ph}_6\text{Pb}_2$ , for a white cloudiness appears at an intermediate stage<sup>3-6</sup>;  $\text{Ph}_3\text{PbCl}$  prepared<sup>8</sup> from  $(\text{NH}_4)_2\text{PbCl}_6$  is inert<sup>9</sup> toward Li metal in THF.

Liquid  $\text{NH}_3$  is a solvent for the formation of  $\text{R}_3\text{PbNa}$  (R = Me, Et, Ph, p-tolyl, p-ethoxyphenyl, o-methoxyphenyl, cyclohexyl) according to Eq. (a)<sup>10-14</sup>. The presence of  $\text{Ph}_3\text{PbNa}$  in the solution is deduced by its conversion to  $\text{R}_3\text{R}'\text{Pb}$  (R' = benzyl) on addition of R'Cl to the reaction mixture<sup>10-12</sup>.

When  $\text{Ph}_2\text{PbCl}_2$  reacts with Li metal in liq  $\text{NH}_3$  a red soln is formed<sup>15</sup> which with EtBr gives  $\text{Ph}_2\text{Et}_2\text{Pb}$ , evidence for the intermediate formation of  $\text{Ph}_2\text{PbLi}_2$ :



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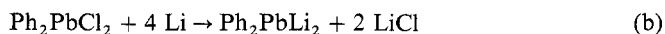
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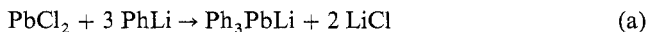
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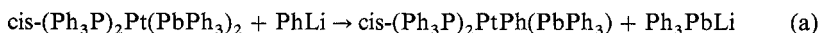
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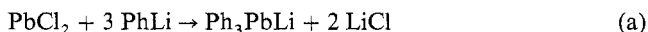
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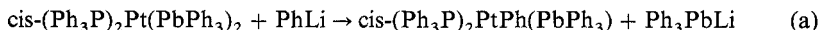
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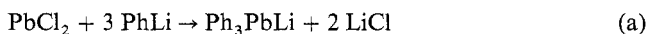
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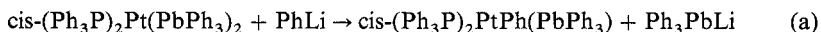
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Triethyllead sodium is an intermediate during reduction of ethyl halides on Pb cathodes in the presence of  $\text{Na}^+$  ions<sup>2</sup>.

(F. HUBER, K. GRÄTZ)

1. B. Crociani, M. Nicolini, D. A. Clemente, G. Bandoli, *J. Organomet. Chem.*, **49**, 249 (1973).
2. O. R. Brown, K. Taylor, H. R. Thirsk, *Electroanal. Chem. Interfac. Electrochem.*, **53**, 261 (1974).

## **5.6. Formation of Bonds between Elements of Group IVB (C, Si, Ge, Sn, Pb) and Group IB (Cu, Ag, Au)**

### **5.6.1. Introduction**

In this chapter are found the reactions used to prepare the coinage-metal (Cu, Ag and Au) derivatives of the main fourth-group elements. Few compounds containing group-IB bonds to the lower congeners of group IVB (Si, Ge, Sn or Pb) can be isolated except for the binaries, and the preparations of these compounds are mentioned together with those of the organic derivatives. Organocopper reagents play an important role in organic synthesis.

(J. J. ZUCKERMAN, ED.)

### **5.6.2. from the Elements.**

Little work on intermetallic phases has relevance for inorganic chemistry.

Nineteenth-century chemists produced binary Si-Cu alloys by heating together carbon (C), Silicon (Si), and copper (Cu) to white heat in closed crucibles to obtain an alloy containing 2.3 wt% Si (the proportion of Si could be increased by heating the elements together at 1200°C for 2 h); or by reductive processes, such as the electrolysis of potassium fluorosilicate with molten Cu metal as the cathode; or by heating together elemental Si and CuO or from  $\text{CuO} + \text{CaO} + \text{C} + \text{SiO}_2$ . The freezing curve for the Cu-Si system shows a maximum at ca. 13 wt% Si (855°C) corresponding to the compound CuSi and two eutectic points at 825° (9.8% Si) and 800°C (18.3% Si). Other binary compounds identified are  $\text{SiCu}_5$ ,  $\text{SiCu}_6$  and  $\text{Si}_4\text{Cu}_{15}$ , all of which melt between 800° and 855°C and have a metallic appearance<sup>1,2</sup>. With Ag and Au, Si forms eutectics, but no binary compounds. The solubility of elementary Si in molten Ag metal is ca. 30% at 1400°C. Gold metal and elementary Si are totally miscible when liquid; the eutectic, containing 6% Si, melts at 370°C.

Like Si, Ge forms a compound  $\text{GeCu}_3$ . Germanium-metal compounds and alloys are listed in ref. 3. Gaseous molecules of the Au-Ge systems are found using a high-T cell in a single-focusing mass spectrometer<sup>4</sup>. Knowledge of metal-cluster geometry leads to predictions of catalytic effects. The vaporization enthalpies and equilibrium pressures of elementary Ge and Au metal are similar and hence likely to lead to large intermetallic clusters. Ionic species observed for this system are:  $[\text{AuGe}]^+$ ,  $[\text{Au}_2\text{Ge}]^+$ ,  $[\text{AuGe}_2]^+$ ,  $[\text{Au}_2\text{Ge}_2]^+$ ,  $[\text{AuGe}_3]^+$  and  $[\text{AuGe}_4]^+$ , and thermal functions for these ions can be calculated. A symmetrical structure is proposed for  $\text{Au}_2\text{Ge}$ , and  $\text{AuGe}_2$  has an asymmetric structure. A similar range of ions is observed for the Sn-Au<sup>5</sup> and Ge-Cu<sup>6</sup> systems at 1525°C.

The Cu-Sn system shows only one compound,  $\text{SnCu}_3$ , mp ca.  $720^\circ\text{C}$ , which is dark- or bluish-grey and is only slowly attacked by HCl and other mineral acids. Melting together Sn and Cu metals forms the 2:1 alloy, after treatment with conc HCl. The molten metals Sn and Ag are soluble in all proportions, but only one compound,  $\text{SnAg}_3$ , is formed. The Sn-Au system shows a eutectic at 20% Sn, mp  $280^\circ\text{C}$ , and the compound  $\text{SnAu}$  (mp  $418^\circ\text{C}$ ), which is silver grey, is only slowly attacked by aqua regia and is resistant to other mineral acids. Other Sn-Au compounds are  $\text{Sn}_2\text{Au}$  and  $\text{SnAu}_4$ .

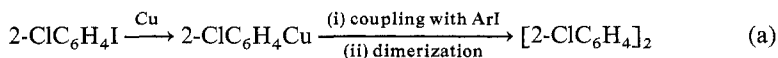
The Cu-Pb system gives a eutectic at  $969^\circ\text{C}$  (60% Pb), but with no evidence for binary compounds. Liquid Ag and Pb metals are miscible in all proportions, but no compounds are identified. By contrast, Au and Pb metals form  $\text{PbAu}_2$  and  $\text{Pb}_2\text{Au}$ , the latter as brittle white crystals.

(F. GLOCKLING)

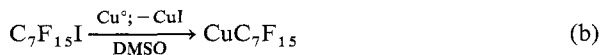
1. A. S. Berezhnoi, *Silicon and Its Binary Systems*, Consultants Bureau, New York, 1960.
2. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 6, Longmans Green, London, 1925.
3. G. V. Samsonov, V. N. Bondarev, *The Germanides*, Metallurgy, Moscow, 1968.
4. J. E. Kingcade, U. V. Choudary, K. A. Gingerich, *Inorg. Chem.*, **11**, 3094 (1979).
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6. H. Sakao, J. F. Elliot, *Metall. Trans.*, **5**, 2383 (1973).

### 5.6.3. from the Group-IB Metals and Alloys.

General synthetic methods for preparing group-IB compounds containing a group-IB-carbon bond directly from the group-IB metals and organic compounds are not available. An obvious reason for Cu and Ag is the low intrinsic stability of the Cu—C and Ag—C bonds<sup>1</sup>, which contrasts with the often forcing conditions required for such reactions. However, synthetically important reactions are known that are based on the use of metallic Cu. In these reactions organocopper compounds are formed as intermediate or transient species that react further with other substrates present in the reaction mixture. Examples include the synthesis of biaryls<sup>2</sup> from aryl halides and Cu metal:



and the synthesis of perfluoroalkyl or -arylcopper compounds in dipolar aprotic solvents such as dimethylsulfoxide (DMSO)<sup>3,4</sup>:



Highly reactive Cu metal from  $\text{Cu}(\text{PEt}_3)\text{I}$  and  $\text{Li}^+[\text{C}_{10}\text{H}_8]^-$  in tetrahydrofuran (THF) can oxidatively add to non-fluorinated organic halides, e.g., to  $\text{PhCH}=\text{CHBr}$  or  $\text{o-O}_2\text{NC}_6\text{H}_4\text{I}$  to give the corresponding Cu derivatives<sup>5</sup>.

Organic halides react with metallic Ag, e.g.,  $\text{Ph}_3\text{CCl}$  with Ag foil<sup>6</sup>, but the organosilver compounds cannot be isolated.

(G. VAN KOTEN)

1. G. van Koten, J. G. Noltes, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Vol. 1, Pergamon Press, Oxford, 1982, Ch. 14, p. 709.

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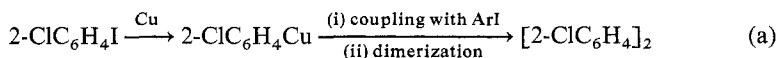
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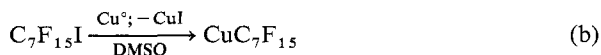
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2. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 6, Longmans Green, London, 1925.
3. G. V. Samsonov, V. N. Bondarev, *The Germanides*, Metallurgy, Moscow, 1968.
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Highly reactive Cu metal from  $\text{Cu}(\text{PEt}_3)\text{I}$  and  $\text{Li}^+[\text{C}_{10}\text{H}_8]^-$  in tetrahydrofuran (THF) can oxidatively add to non-fluorinated organic halides, e.g., to  $\text{PhCH}=\text{CHBr}$  or  $\text{o-O}_2\text{NC}_6\text{H}_4\text{I}$  to give the corresponding Cu derivatives<sup>5</sup>.

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2. M. Nilsson, *Acta Chem. Scand.*, **12**, 537 (1958) [cf. R. G. R. Bacon, H. A. O. Hill, *Chem. Soc. Rev.*, **19**, 95 (1965); an extensive review].
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4. J. Burdon, P. L. Coe, C. R. Marsh, J. C. Tatlow, *J. Chem. Soc., Perkin Trans.*, **1**, 639 (1972).
5. G. W. Ebert, R. D. Rieke, *J. Org. Chem.*, **49**, 5280 (1984).
6. H. Dunken, H. Hobert, K. Schmidt, cited in *Gmelin Handbuch der Anorganische Chemie, Silber*, by R. Keim, Teil B5, Springer-Verlag, Berlin, 1974.

### 5.6.4. from the Metal Salts

For the preparation of pure organometallic-IB compounds, the following points<sup>1</sup> should be considered:<sup>7</sup>

1. Of the various possibilities for the group IB-group IVB bond, only the synthesis of compounds containing a  $\sigma$  or  $\eta^2$  bond between the group-IB metal and the one-electron (e.g., Me, Ph,  $\text{C}\equiv\text{CR}$ ) or two-electron (e.g., CO, olefin) carbon ligands is known in detail. The synthesis of  $\eta^2$ -metal IB-carbon-containing compounds is discussed in §5.6.2.3.6.
2. Organocopper compounds are known for Cu(I) but not for Cu(II); organosilver compounds contain Ag(I), whereas organogold compounds are synthesized for both Au(I) and Au(III).
3. The stability of the  $\sigma$ -metal IB-carbon bond follows the order alkyl-M < aryl-M  $\sim$  alkenyl-M < alkynyl-M [M = Cu(I), Ag(I), Au(I)L]. However, for Cu(I) and Ag(I), most alkyl, aryl and alkenyl compounds are only stable at  $<0^\circ\text{C}$ <sup>1</sup>. Furthermore, the stable organogold(I) species, with a few exceptions, have the general formula  $\text{RAu(I)L}$ , in which L is a neutral two-electron donor ligand.
4. Organocopper and -silver compounds are susceptible to hydrolysis and oxidation, whereas organogold(I) and -gold(III) compounds have good hydrolytic and oxidative stability. The Ag compounds, moreover, are often light sensitive<sup>2</sup>. The organocopper(I) and -silver(I) compounds often have low solubility. This adds to the problem of obtaining pure compounds.
5. Despite their limited thermal stability, organocopper compounds are reagents in organic synthesis and have advantages over the usually applied organolithium and organomagnesium-halide reagents<sup>1</sup>. In these syntheses the organocopper compounds are reacted further without prior isolation. These reactions are not discussed here. Reviews are available<sup>3-7</sup>.
6. Reviews that contain pertinent information concerning the synthesis and structures of organometal-IB compounds are available. For  $\sigma\text{-M}-\text{C}$ -containing compounds, see refs. 1-3, 7-13, and for  $\eta^2\text{-M}-\text{C}$  compounds, refs. 2, 8, 14-16. Examples of stable, well-characterized organometal-IB compounds are given in Table 1. **Solid alkylcopper and -silver compounds, although stable as suspensions at  $-80^\circ\text{C}$ , may decompose spontaneously or even explode. Handling should be carried out only by an experienced person.**

(G. VAN KOTEN)

1. G. van Koten, J. G. Noltes, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Vol. 1, Pergamon Press, Oxford, 1982, Ch. 14, p. 709. Recommended reading for the synthesis and structure relationship of organocopper and -silver compounds.
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2. *Gmelin Handbuch der Anorganischen Chemie, Silber*, Teil B5, Springer-Verlag, Berlin, 1974. Excellent review.

TABLE 1. STABLE, WELL-DEFINED ORGANOMETAL-IB COMPOUNDS<sup>a</sup>

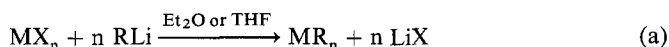
Compound	Synthetic route	Decomposition T (°C)	Ref.
[CuCH <sub>3</sub> SiMe <sub>3</sub> ] <sub>4</sub>	CuI/LiCH <sub>3</sub> SiMe <sub>3</sub>	78–79 (mp)	17
AgCF(CF <sub>3</sub> ) <sub>2</sub> · MeCN	AgF/CF <sub>3</sub> CF = CF <sub>2</sub> in MeCN	> 60	18
Au(I)Me <sub>4</sub> (PPh <sub>3</sub> ) <sub>3</sub>	AuCl(PPh <sub>3</sub> ) <sub>3</sub> /LiMe	175 (mp)	19
Au(III)Me <sub>4</sub> (PPh <sub>3</sub> ) <sub>3</sub>	AuCl <sub>3</sub> /LiMe/PPh <sub>3</sub>	23 (mp)	19
[CuC <sub>6</sub> H <sub>4</sub> Me-n] <sub>4</sub>	CuBr/LiC <sub>6</sub> H <sub>4</sub> Me-n (n = 2 or 4)	≈ 100	20,21
	CuCl/Zn(C <sub>6</sub> H <sub>4</sub> Me-2) <sub>2</sub>		22
[M(C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> -2)] <sub>n</sub>	MBr/LiC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> -2	≈ 160–185	23
n = 4; M = Cu(I), Ag(I)	Au <sub>2</sub> Li <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> -2) <sub>4</sub> /Me <sub>3</sub> SnBr	117	24
n = 2; M = Au(I)			
Au(I)Ph(PPh <sub>3</sub> ) <sub>3</sub>	AuCl(Ph <sub>3</sub> P)/LiC <sub>6</sub> H <sub>5</sub>	152	25
Au(III)(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Cl(PPh <sub>3</sub> )	AuCl(Ph <sub>3</sub> P)/(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> TIr	150	26,27
Ag <sub>2</sub> Au <sub>2</sub> (O <sub>3</sub> SCF <sub>3</sub> ) <sub>2</sub> -(C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> -2) <sub>4</sub>	Au <sub>2</sub> Li <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> -2) <sub>4</sub> /4 Ag(O <sub>3</sub> SCF <sub>3</sub> )	130 (decomp)	28
M <sub>2</sub> Li <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> -2) <sub>4</sub>	MX/2LiR M = Cu(I), Ag(I)	140–200	29
M = Cu(I), Ag(I) or Au(I)	MR/LiR M = Cu(I), Ag(I)		
h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> M(PPh <sub>3</sub> ) <sub>3</sub>	Au(PPh <sub>3</sub> ) <sub>3</sub> (C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> -2)/LiR		29
M = Cu(I), Ag(I), Au(I)	Cu <sub>2</sub> O/C <sub>5</sub> H <sub>5</sub> /PPh <sub>3</sub>		See §5.6.2.3
	MCl/NaC <sub>5</sub> H <sub>5</sub> /PPh <sub>3</sub>		
	[(AuPPh <sub>3</sub> ) <sub>3</sub> O][BF <sub>4</sub> ]/C <sub>5</sub> H <sub>5</sub> /NaH		
Cu <sub>4</sub> R' <sub>4</sub> Br <sub>2</sub> R = C(C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> -2) = C(Me)(C <sub>6</sub> H <sub>4</sub> Me-4)	CuBr/LiR	155	30
AgCH = CHC <sub>6</sub> H <sub>5</sub>	AgNO <sub>3</sub> /Et <sub>3</sub> PbCH = CHPh	> 60 (decomp)	31

<sup>a</sup> The compounds are isolated pure in > 60% yields.

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#### 5.6.4.1. by Metal-Metal Exchange with Another Organometallic.

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where  $n = 1$ ;  $\text{M} = \text{Cu(I)}, \text{Ag(I)}, \text{LAu(I)}$  ( $\text{L} =$  neutral two-electron donor ligand); or  $n = 3$ ;  $\text{M} = \text{Au(III)}$ . These reactions are carried out at  $<0^\circ\text{C}$  with exclusion of moisture,  $\text{O}_2$  and light (for organosilver compounds) (see Table 1, §5.6.2.3). Although  $\text{RMgX}$  reagents also can be applied, the use of organolithium compounds is recommended because these provide the organometallic-IB compounds in better yields and higher purity. Exceptions are the perhaloaryl and the 2,6-disubstituted arylmetal-IB compounds, which proceed well via the  $\text{RMgX}$  route (vide infra).

## 5.6. Formation of Bonds between Elements of Groups IVB and IB

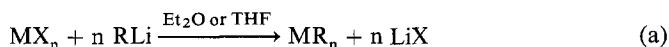
### 5.6.4. from the Metal Salts

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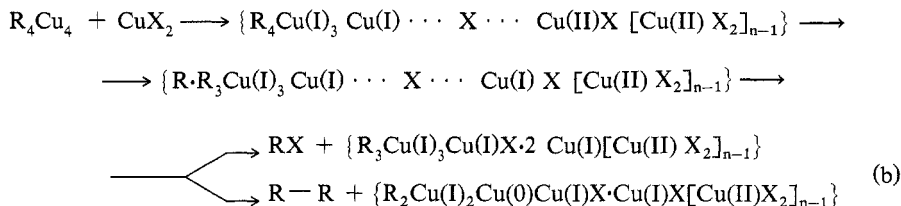


where  $n = 1$ ;  $\text{M} = \text{Cu(I)}, \text{Ag(I)}, \text{LAu(I)}$  ( $\text{L} =$  neutral two-electron donor ligand); or  $n = 3$ ;  $\text{M} = \text{Au(III)}$ . These reactions are carried out at  $<0^\circ\text{C}$  with exclusion of moisture, O<sub>2</sub> and light (for organosilver compounds) (see Table 1, §5.6.2.3). Although  $\text{RMgX}$  reagents also can be applied, the use of organolithium compounds is recommended because these provide the organometallic-IB compounds in better yields and higher purity. Exceptions are the perhaloaryl and the 2,6-disubstituted arylmetal-IB compounds, which proceed well via the  $\text{RMgX}$  route (vide infra).

For the preparation of the organocopper compounds,  $\text{RCu}$ ,  $\text{Cu(I)}$  halides (preferably the bromide) are employed, although  $\text{Cu(I)CN}^1$ ,  $\text{Cu(I)SCN}^1$ ,  $\text{Cu(I)O}_3\text{SCF}_3$  (soluble in benzene!)<sup>2</sup> or the ether-soluble phosphine complexes of these salts [e.g.,  $\text{Cu(I)I[P(Bu-n)}_3\text{]}_4\text{-tetramer}^3$ ] can be used also.

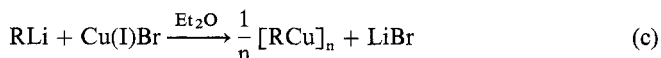
The use of  $\text{Cu(II)}$  salts is not recommended because transmetallation, Eq. (c), is then preceded by reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$ , which requires an extra equivalent of organolithium or  $\text{RMgX}$  reagent. Moreover, the oxidation products of the organo group and the interaction of the newly formed organocopper with unreacted  $\text{Cu(II)X}_2$  can hamper the isolation of pure products. The 1-norbornylcopper which is prepared from  $\text{Cu(II) acac}_2$  and 1-norbornyllithium is an exception<sup>4</sup>.

The  $\text{Cu(II)X}_2\text{-CuR}$  reaction results in formation of oxidative coupling and ligand-transfer oxidation products,  $\text{R-R}$  and  $\text{R-X}$ , respectively, e.g.<sup>5</sup>:

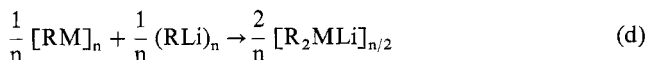


The reaction of  $\text{RCu}$  with  $\text{Cu(II)X}_2$  is useful for the oxidative dimerization of functionalized organo groups<sup>1,6-10</sup>.

For the synthesis of pure organocopper compounds xs organolithium or  $\text{RMgX}$  reagents, as well as of  $\text{Cu}$  salts, must be avoided. The former give rise to cuprate complexes<sup>5</sup>:



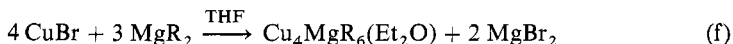
where, e.g.,  $\text{R} = \text{Ph}^{11}$ ,  $\text{C}_6\text{H}_4\text{OMe-2}^{12}$ ,  $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}^{13}$ ,  $\text{C}_5\text{H}_4\text{CH}(\text{SiMe}_3)_2^{14}$ ;



where, e.g.<sup>13</sup>, for  $\text{R} = \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}$  and  $\text{M} = \text{Cu(I)}$  or  $\text{Ag(I)}$ ,  $n = 4$ . Whereas, e.g., pure  $\text{Cu}_4(\text{C}_6\text{H}_4\text{CF}_3\text{-2})_4$  can be obtained<sup>15</sup> from the reaction of the corresponding  $\text{RMgX}$  reagent with  $\text{CuBr}$ , similar reactions of phenylmagnesium halides with  $\text{CuBr}$  give mixtures of products with complex  $\text{Ph}:\text{Cu}:\text{MgX}_2$  ratios<sup>16</sup>:



where e.g.<sup>15</sup>,  $\text{R} = \text{C}_6\text{H}_4\text{CF}_3\text{-2}$ ,  $\text{C}_6\text{F}_5$ ;

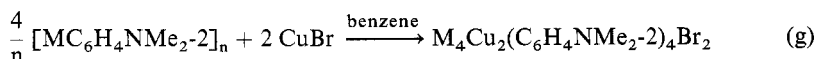


where  $\text{R} = \text{Ph}$ ,  $\text{C}_6\text{H}_4\text{Me-4}$ . The cuprate species in Eq. (f) is identified by using xs  $\text{R}_2\text{Mg}$  reagent<sup>17,18</sup>.

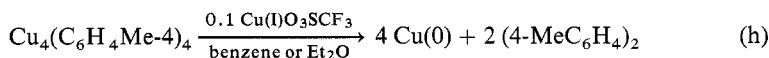
The cuprate complexes have better thermal stability and solubility than the parent organocopper compounds. They can be prepared directly in high yields from the 2:1 reaction of  $\text{RLi}$  with  $\text{CuBr}$  [Eqs. (c) + (d)]<sup>5,13</sup> or quantitatively via the 1:1 reaction of

pure RLi with the pure RCu species [Eq. (d)]<sup>13</sup>. The alkylcopperlithium species, Alk<sub>4</sub>-Cu<sub>4-n</sub>Li<sub>n</sub>, are synthetic intermediates for mediating new C—C bonds, often in a stereoselective and regioselective coupling manner (see refs. 1–16, §5.6.2.3). The solution structures of M<sub>2</sub>Li<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)<sub>4</sub> [M = Cu(I), Ag(I) or Au(I)], which are isolated pure, are studied by <sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li and <sup>109</sup>Ag NMR spectroscopy<sup>15,19</sup>. Phenyllithium reacts with CuBr in THF to give low yields of [Cu<sub>5</sub>Ph<sub>6</sub>]<sup>–</sup> anionic clusters and [Li(THF)<sub>4</sub>]<sup>+</sup> cations<sup>20</sup>. Mononuclear [bis(alkyl)copper]Li<sup>+</sup> complexes are formed<sup>21</sup> with bulky alkyl groups, e.g., [Li(THF)<sub>4</sub>][Cu{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>]. Reactions of polynuclear arylcoppers, in which the aryl group is substituted in both ortho positions (e.g., mesityl), with bidentate ligands (e.g., diphos) may lead<sup>22</sup> to mononuclear bisaryl copper anion-bis(ligand)copper cation complexes (e.g., [Cu(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)<sub>2</sub>][Cu 2 dihos]). With terdentate phosphine ligands, mononuclear arylcopper compounds are formed, e.g., Cu(triphos)Cl with PhLi in THF provides Cu(triphos)Ph in 60 % yield<sup>23</sup>.

Reactions of the organolithium compounds with xs Cu(I) salts may lead either to formation of polynuclear organocopper–copper salt complexes<sup>24</sup>:



where M = Cu(I), Ag(I), or to catalytic decomposition<sup>25</sup>:



The organocopper–copper salt complexes synthesized via Eq. (g) are stable, have a well-defined stoichiometry and can be isolated in high yields<sup>24</sup>. With 2 equiv of LiC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2, the compound [M = Cu(I)] can be converted<sup>24</sup> into pure CuC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2 (see also §5.6.2.3.1.ii). However, in the reaction of ViLi [Vi is (E)-(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)C≡C(Me)(C<sub>6</sub>H<sub>4</sub>Me-4)] with CuBr, this alkenylcopper–copper salt complex, [Cu<sub>4</sub>Br<sub>2</sub>Vi<sub>2</sub>], is the stable end product<sup>26</sup> (see also §5.6.2.3.1.ii). However, complex formation with metal salts (also MgX<sub>2</sub>) is often less specific and leads to mixtures of inseparable products.

The counteranion can determine the stability of the organocopper formed. p-Tolylcopper tetramer synthesis via the RLi–CuO<sub>3</sub>SCF<sub>3</sub> route is impossible<sup>25</sup>; whereas it can be accomplished in 50 % yield when CuBr is used<sup>25</sup>. This difference is ascribed to the p-tolylcopper–copper trifluoromethane sulfonate intermediates, which are unstable. Stable, mixed (organo)(organic)Cu species, e.g., Cu<sub>3</sub>(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)(O<sub>2</sub>CPh)<sub>2</sub>, can be prepared via the interaggregate exchange between mesitylcopper pentamer<sup>27</sup> and copper benzoate dimer.

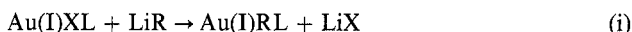
For those reactions covered by Eqs. (c) and (e), the order of addition of the organolithium or organomagnesium-halide reagents and the starting Cu salts may affect the nature and purity of the organocopper products (cf. ref. 4 for a discussion and examples).

Treatment of CuCl with LiC<sub>5</sub>Me<sub>5</sub> in THF at –78°C affords a CuC<sub>5</sub>Me<sub>5</sub>-h<sup>5</sup> reagent that is used for the synthesis of transition-metal cluster species containing the CuC<sub>5</sub>Me<sub>5</sub>-h<sup>5</sup> fragment<sup>28–30</sup>.

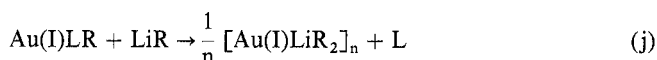
The metal–metal exchange reaction (a) also can be applied to the synthesis of pure organosilver compounds<sup>1</sup>. The available AgNO<sub>3</sub> should not be used as a starting

material because of its complex formation with the organosilver product [e.g.,  $\text{AgMe} \cdot \text{AgNO}_3$ ,  $(\text{AgPh})_n(\text{AgNO}_3)_m$ ,  $n/m = 2$  or  $5/2$ ; see ref. 2, §5.6.2.3]. Instead, reactions of the organolithium compound with  $\text{AgBr}$  give better yields and pure products<sup>31</sup>. The problems mentioned above concerning possible complexation of organosilver species with either silver salts [Eq. (g) and, e.g., formation<sup>31</sup> of  $[\text{AgC}_6\text{H}_4\text{CH}_2\text{NMe}_2 \cdot 2 \cdot \text{AgBr}]$  or with xs organolithium reagent [cf. Eq. (d), e.g., preparation<sup>32</sup> of  $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$  and of<sup>33</sup>  $[\text{Ag}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$  are valid not only for the synthesis of organocoppers, but for the preparation of pure organosilver compounds as well.

The pure and stable organogold (I) compounds,  $\text{RAuL}$ , can be prepared starting from a gold(I) halide-ligand complex<sup>34-42</sup>:



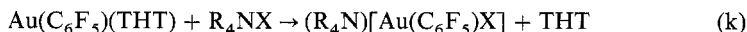
where, e.g.,  $\text{R} = \text{Me}$ ,  $\text{Ph}$ ,  $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2 \cdot 2$ ;  $\text{L} = \text{PPh}_3$ , tetrahydrothiophene (THT);



where, e.g.,  $\text{R} = \text{Me}$ <sup>40,41</sup>,  $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2 \cdot 2$ <sup>19</sup>,  $\text{L} = \text{PPh}_3$ .

These reactions can be carried out at RT. Isolation of the  $\text{RAuL}$  complexes is easier than for the corresponding  $\text{RCu}$  or  $\text{RAg}$  complexes because of the better solubility of the  $\text{Au(I)}$  derivatives in organic solvents and their better thermal stability. However, use of xs organolithium or  $\text{RMgX}$  reagent causes aurate complexes, [cf. Eq. (j)] to form. Pure  $[\text{AuLiR}_2]$  complexes can be isolated from displacement reactions<sup>15,40,41</sup> of the neutral ligand by  $[\text{R}]^-$ . This reaction sequence also provides a route for the preparation of ligand-free  $\text{RAu(I)}$  complexes<sup>39</sup>, vide infra, e.g., Eq. (n).

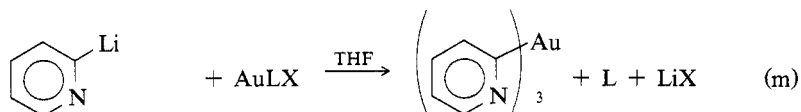
When weak coordinating ligands,  $\text{L}$ , such as  $\text{Ph}_3\text{As}$  or THT are used, anionic haloarylgold(I) compounds can be synthesized starting from  $\text{AuRL}$  complexes<sup>42,43</sup>:



or from the  $\text{Au(I)}$ -halide complex<sup>43</sup>:



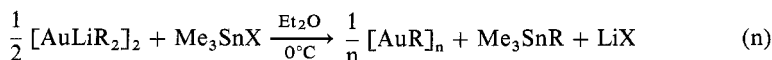
Stable complexes  $(\text{AuR})_n$  are obtained when the aryl group  $\text{R}$  contains a suitably positioned heteroatom from which intermolecular coordination to  $\text{Au(I)}$  can occur<sup>39,42</sup>:



where  $\text{L} = \text{AsPh}_3$ <sup>44</sup>, THT<sup>42</sup>.

A prerequisite for the occurrence of this reaction is the use of weakly coordinating ligands in the starting  $\text{AuLX}$  complex.

An alternative route makes use of the different reactivity of the metal  $\text{IB}-\text{C}$  and  $\text{Li}-\text{C}$  bonds toward the arylation of triorganotin halides; reaction (j), in which the ligand  $\text{L}$  is removed, is then followed by:

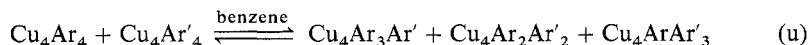




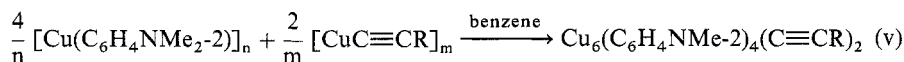
Treatment of  $[\text{AuCl}_4][\text{NMe}_4]$  with  $\text{R}_2\text{Mg}$  derivatives ( $\text{R} = \text{C}_6\text{H}_4\text{NO}_2$ -2 or  $\text{C}_6\text{H}_3\text{Me}$ -2- $\text{NO}_2$ -6) gives the aromatic  $\text{Au}(\text{III})$  complexes<sup>43</sup>  $[\text{cis-AuR}_2\text{Cl}_2][\text{NMe}_4]$ .

(ii) Via Interaggregate Exchange and Ligand Substitution. These two routes are important for the synthesis of polynuclear organometallic-IB compounds. Interaggregate exchange between tetranuclear organocopper or -silver compounds and the corresponding tetranuclear organolithium compound leads to quantitative formation of the mixed Cu-Li and Ag-Li species, respectively [see Eq. (d), §5.6.2.3.i.<sup>13,50,51</sup>].

Mixed arylcopper compounds can be prepared via reaction of two pure organocopper compounds<sup>51,52</sup>:

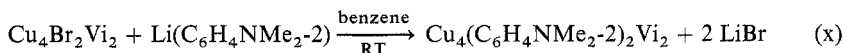
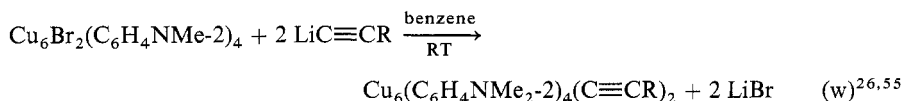


where Ar = C<sub>6</sub>F<sub>5</sub> or C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2; Ar' = C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-2 or C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>NMe<sub>2</sub>-2-Me-5. However, the tetrameric species cannot be separated. A pure mixed-copper species is formed by reacting an aryl and an alkynylcopper compound<sup>51,52</sup>:



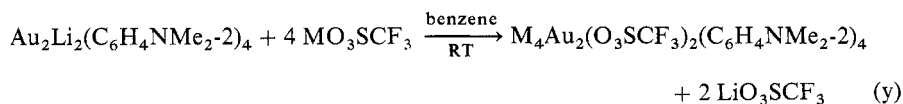
Mixed copper-silver compounds are obtained by reacting AgC<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub> with CuI; CuAg[C<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub>]<sub>2</sub> is isolated in 63 % yield<sup>53</sup>. A similar reaction between AgC<sub>6</sub>F<sub>5</sub> and CuI produces<sup>54</sup> AgI and CuC<sub>6</sub>F<sub>5</sub> quantitatively.

The halogen atoms in the mixed arylhalogen-Cu clusters react with organolithiums with the formation of Cu-C bonds. These substitutions take place with retention of the cluster structure:



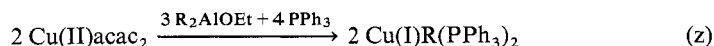
where Vi = vinyl.

Compounds consisting of aryl groups and anionic atoms (Br, I) or groups (O<sub>3</sub>SCF<sub>3</sub>) bound to a polynuclear array of Ag(I) and Au(I) or Au(I) and Cu(I) atoms can be prepared in 90 % yield<sup>2,24,39</sup>:

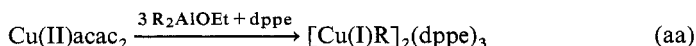


where M = Cu(I), Ag(I).

(iii) Via Organoaluminiums. Organoaluminium reagents react with Cu(II) acetylacetonate in the presence of phosphines to give the corresponding alkylcopper(I) phosphine complexes<sup>56</sup>:

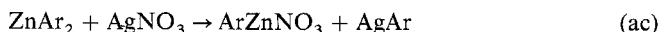
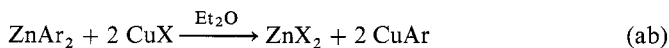


where R = Me, Et, n-Pr, i-Bu;



where R = Me, Et, n-Pr, i-Bu and dppe is bis(diphenylphosphino)ethane,  $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2)\text{PPh}_2$ .

(iv) Via Reaction with Organozincs. Dialkylzinc compounds can be used to prepare pure alkylcoppers. Although the method starts from Cu(II) halides<sup>57</sup>, better yields and higher purity of the insoluble alkylcoppers are obtained when Cu(I) halides are used. The synthesis of arylcoppers via diarylzincs is claimed as a route to pure compounds<sup>58</sup>:

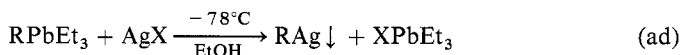


where Ar = Ph,  $\text{C}_6\text{H}_4\text{Me-}n$  ( $n = 2, 3, 4$ ),  $\text{C}_6\text{H}_3\text{Me}_2\text{-}2,6$ . However, when the aryl group contains coordinating substituents, purification of the arylcopper from the zinc halides formed is difficult [see §5.6.2.3.1.i, synthesis via the organolithium route (above)].

Arylsilvers are quantitatively formed in the 1 : 1 reaction of finely divided  $\text{AgNO}_3$  in ether with diarylzinc and can be isolated pure<sup>59,60</sup>.

The synthesis of pure organogold compounds via the Zn route is not important. Reaction of  $\text{Au(III)Cl}_3$  or  $\text{Au(I)(CO)Cl}$  with xs diphenylzinc affords the  $\text{AuZnPh}_3$  dimer in good yield, whereas the 1 : 1 reaction produces<sup>61</sup>  $\text{Ph}_2\text{AuZnCl}$ <sup>61</sup>. Addition of  $\text{ZnPh}_2$  to  $\text{Au(III)PhCl}_2$  dimer in the presence of  $\text{PPh}_3$  gives  $\text{Au(I)Ph(PPh}_3)$  in good yields<sup>61</sup>.

(v) Via Tetraorgano Group-IV Compounds. The synthesis of alkylcoppers via reaction of tetraalkylleads with Cu(II) salts is possible but impracticable when pure products are wanted<sup>62,63</sup>. Likewise, alkylsilvers are formed in the 1 : 1 reaction of  $\text{AgNO}_3$  with tetraalkylleads in MeOH at low T. However, isolation of the alkylsilver derivative is impossible<sup>64,65</sup>. Alkenylsilver compounds, which are more thermally stable than the alkylsilver compounds, are isolated in moderate yields from reactions of the alkenyl-triethylleads with  $\text{AgNO}_3$  at  $-78^\circ\text{C}$  in EtOH<sup>64,65</sup>:



where, e.g., R = isobutenyl, styryl<sup>66</sup>.

Pure, uncomplexed phenylsilver can be isolated in good yields from the reaction in which  $\text{AgNO}_3$  in EtOH is slowly added to a soln of xs trialkylphenyltins or -leads at  $>15^\circ$  and  $>-10^\circ\text{C}$ , respectively<sup>67</sup>.

The synthesis of organocopper or -silver compounds via tetraorgano group-IV compounds is inferior to routes involving the use of organolithiums.

(vi) Via Organothalliums. Organothalliums are transmetallation reagents for the synthesis of organocopper and -silver compounds. However, their potential is for organogold synthesis, and the derivatization of these compounds, in particular the making of organogold(III) compounds.

Examples in organocopper chemistry are the synthesis of  $\text{h}^5$ -cyclopentadienyl-copper complexes with phosphite, phosphine or isocyanide ligands via the reaction of  $\text{h}^5\text{-C}_5\text{H}_5\text{Ti}$  with Cu(I) halide-ligand complexes in pentane or THF at  $25^\circ\text{C}$ <sup>68</sup>.

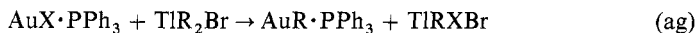


Correspondingly  $\text{Ag(PPh}_3)\text{C}_5\text{H}_5\text{-h}^5$  can be isolated from the 1:1 reaction of  $\text{AgO}_3\text{SCF}_3$  with  $\text{NaC}_5\text{H}_5$  in THF<sup>69</sup>.

Organothalliums transfer aryl groups to Au(I) or Au(III) centers. An exception is the synthesis of C-bonded acetylacetonate via<sup>40,70,71</sup>:

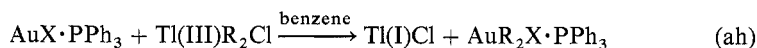


Transfer of perhaloaryl groups from Ti(III) (either as  $\text{R}_3\text{Ti}$  or as  $\text{R}_2\text{TiCl}$ ) to Au(I) is possible without oxidation<sup>72,73</sup>:



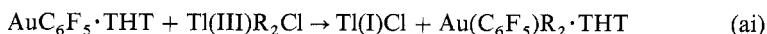
where, e.g.,  $\text{R} = \text{C}_6\text{F}_5$ ;  $\text{X} = \text{Ph}$ ,  $\text{NO}_3$ ,  $\text{MeCO}_2$ . For  $\text{X} = \text{Ph}$  this reaction involves exchange of aryl groups. The monoarylthalliums formed in Eq. (ag) are further converted to the more stable diarylthallium halides.

The influence of the counterion in the starting Au(I) complex is demonstrated by:



where  $\text{X} = \text{Cl}$ ;  $\text{R} = \text{C}_6\text{F}_5$ , 2,4,6- $\text{F}_3\text{H}_2\text{C}_6$ . When reaction (ag),  $\text{X} = \text{Cl}$ , is carried out in refluxing benzene, oxidation occurs and the diaryl Au(III) complexes are obtained<sup>74</sup>. However, no reaction occurs<sup>74</sup> with  $\text{R} = \text{C}_6\text{H}_4\text{F}-4$  and  $\text{C}_6\text{H}_4\text{CF}_3-3$ .

The use of weak coordinating ligands opens up a route to mixed triarylgold(III) derivatives, which for various R groups can be isolated in high yields<sup>74</sup>:

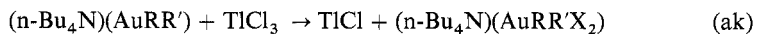
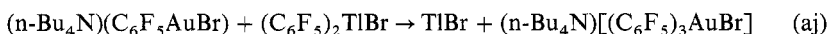


where  $\text{R} = \text{C}_6\text{H}_2\text{F}_3-2,4,6$ . These complexes react readily with neutral ligands, such as  $\text{PPh}_3$ ,  $\text{AsPh}_3$  or bis(diphenylphosphine)methane, to give the corresponding Au(III) $\text{R}_3\text{L}$  complexes<sup>75</sup>.

In the Ti route for organogold synthesis, although no reaction occurs between  $\text{Au(I)(C}_6\text{F}_5)_2\text{PPh}_3$  and  $\text{Ti(III)(C}_6\text{F}_5)_2\text{Br}$ , reaction with  $\text{TiCl}_3$  results in electron transfer and halide exchange, affording<sup>76</sup>  $\text{cis-C}_6\text{F}_5\text{Au(III)Cl}_2 \cdot \text{PPh}_3$ .

In this reaction it is advisable to use Au and Ti species containing similar anions because, otherwise, mixtures of products with different anions can be obtained.

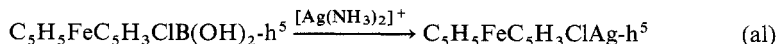
A series of organogold compounds can be made starting from anionic Au(I) complexes and reacting these with diarylthallium bromides<sup>43,77</sup>:



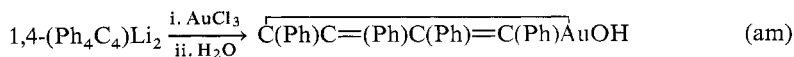
where  $\text{R} = \text{R}' = \text{C}_6\text{F}_5$ ,  $\text{C}_6\text{H}_2\text{F}_3-2,4,6$ ;  $\text{R} = \text{C}_6\text{F}_5$ ,  $\text{R}' = \text{C}_6\text{H}_2\text{F}_3-2,4,6$ .

(vii) Via Other Organometallics. Organometal-IB compounds are formed by using organometallics other than the previously mentioned Li, Mg or Ti derivatives. Although these reactions are isolated examples, they are described briefly here because they may have wider applicability.

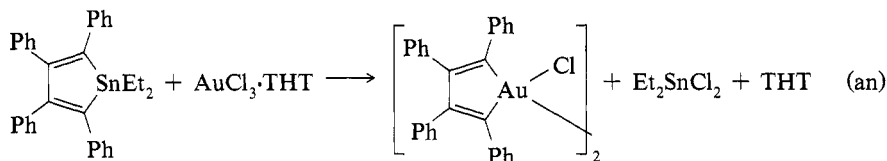
Reaction of ferrocenylboronic acid with  $\text{Ag}^+$  ions affords the corresponding ferrocenylsilver complex<sup>78</sup>:



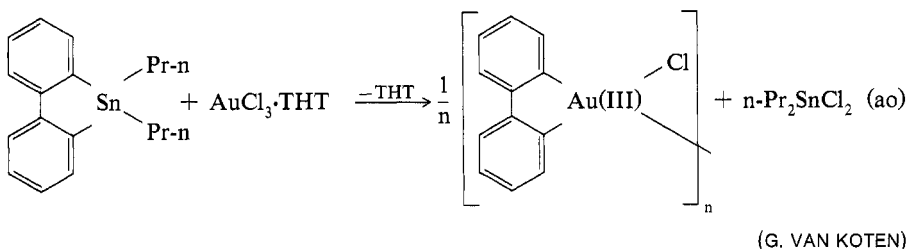
A 1-auracyclopentadiene complex can be prepared via the organolithium route<sup>79</sup>:



However, similar 1-auracyclopentadiene complexes are synthesized (75% yield) by reaction of the diethylstannole derivative with  $\text{AuCl}_3 \cdot \text{THT}$  in ether<sup>80</sup>:



Other metallocyclic tin compounds react similarly, producing the metallocyclic Au(III) derivatives<sup>81,82</sup>:



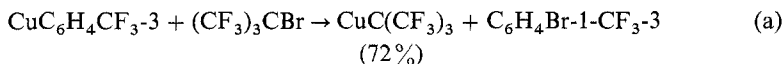
1. See refs. 1-3, 7-10 of §5.6.2.3.
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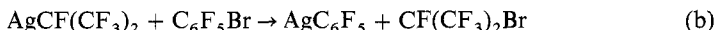
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#### 5.6.4.2. by Metal-Halogen Exchange.

Metal IB-halogen exchange reactions are of limited value in organometal-IB synthesis. A notable exception in organocopper synthesis is the preparation of perfluoro-t-butylcopper<sup>1</sup>:



The reverse reaction can be carried out in organosilver chemistry<sup>2</sup>:



These metal-halogen exchange reactions, i.e.:



where X = Br, I, follow the order<sup>2</sup>:  $\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)$  displaces  $\text{C}_6\text{F}_5$ , which displaces  $(\text{CF}_3)_2\text{CF}$ .

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#### 5.6.4.3. by Metallation.

Alkynylmetal-IB compounds are more stable than the alkyl- or arylmetal-IB compounds. The Cu compounds can be prepared via a reaction of the alkyne with ammoniacal Cu(I) chloride:



These compounds are formed quantitatively and are obtained pure because of their insolubility<sup>1-3</sup>.

Preparation of  $\text{CuC}\equiv\text{CPh}\cdot\text{L}$  (L=1,10-phen, bipy) occurs by oxidation of  $\text{HC}\equiv\text{CPh}$  in acetone or  $\text{CH}_3\text{CN}$  at a Cu anode<sup>4</sup>. Treatment of  $\text{CuBH}_4(\text{PPh}_3)_2$  with  $\text{HC}\equiv\text{CPh}$  and KOH affords tetranuclear  $[\text{CuC}\equiv\text{CPh}(\text{PPh}_3)]_4$  in high yield<sup>5</sup>.

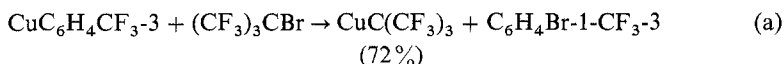
## 5.6. Formation of Bonds between Elements of Groups IVB and IB 229

### 5.6.4. from the Metal Salts

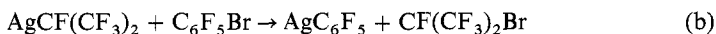
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These metal-halogen exchange reactions, i.e.:



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Alkynylmetal-IB compounds are more stable than the alkyl- or arylmetal-IB compounds. The Cu compounds can be prepared via a reaction of the alkyne with ammoniacal Cu(I) chloride:



These compounds are formed quantitatively and are obtained pure because of their insolubility<sup>1-3</sup>.

Preparation of  $\text{CuC}\equiv\text{CPh}\cdot\text{L}$  (L=1,10-phen, bipy) occurs by oxidation of  $\text{HC}\equiv\text{CPh}$  in acetone or  $\text{CH}_3\text{CN}$  at a Cu anode<sup>4</sup>. Treatment of  $\text{CuBH}_4(\text{PPh}_3)_2$  with  $\text{HC}\equiv\text{CPh}$  and KOH affords tetranuclear  $[\text{CuC}\equiv\text{CPh}(\text{PPh}_3)]_4$  in high yield<sup>5</sup>.



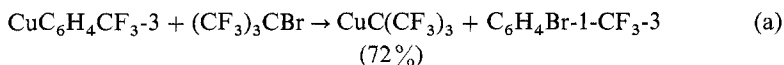
## 5.6. Formation of Bonds between Elements of Groups IVB and IB 229

### 5.6.4. from the Metal Salts

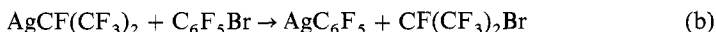
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#### 5.6.4.2. by Metal-Halogen Exchange.

Metal IB-halogen exchange reactions are of limited value in organometal-IB synthesis. A notable exception in organocopper synthesis is the preparation of perfluoro-*t*-butylcopper<sup>1</sup>:



The reverse reaction can be carried out in organosilver chemistry<sup>2</sup>:



These metal-halogen exchange reactions, i.e.:



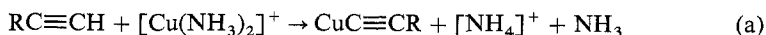
where X = Br, I, follow the order<sup>2</sup>:  $\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)$  displaces  $\text{C}_6\text{F}_5$ , which displaces  $(\text{CF}_3)_2\text{CF}$ .

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#### 5.6.4.3. by Metallation.

Alkynylmetal-IB compounds are more stable than the alkyl- or arylmetal-IB compounds. The Cu compounds can be prepared via a reaction of the alkyne with ammoniacal Cu(I) chloride:



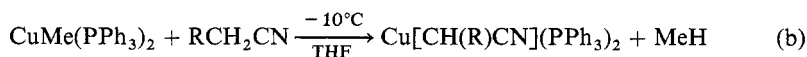
These compounds are formed quantitatively and are obtained pure because of their insolubility<sup>1-3</sup>.

Preparation of  $\text{CuC}\equiv\text{CPh}\cdot\text{L}$  (L=1,10-phen, bipy) occurs by oxidation of  $\text{HC}\equiv\text{CPh}$  in acetone or  $\text{CH}_3\text{CN}$  at a Cu anode<sup>4</sup>. Treatment of  $\text{CuBH}_4(\text{PPh}_3)_2$  with  $\text{HC}\equiv\text{CPh}$  and KOH affords tetranuclear  $[\text{CuC}\equiv\text{CPh}(\text{PPh}_3)]_4$  in high yield<sup>5</sup>.

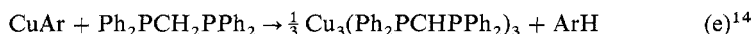
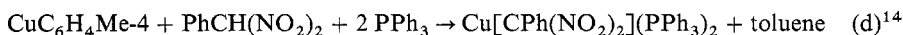
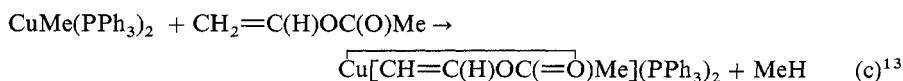
Reaction of alkynes with  $\text{AgNO}_3$  or  $\text{AgClO}_4$  in alcohols or  $\text{H}_2\text{O}$  in the presence of  $\text{NH}_3$  results similarly in alkynylsilver(I) compounds quantitatively. When xs  $\text{AgNO}_3$  is used and the reaction is performed in neutral solution, complex formation between alkynylsilver and  $\text{AgNO}_3$  takes place. The ratio  $\text{AgNO}_3 : \text{AgC}\equiv\text{CR}$  in these complexes depends on the  $\text{AgNO}_3$  concentration during the reaction<sup>2,3,6,7</sup>.

The alkynylgold(I) compounds  $\text{AuC}\equiv\text{CR}$  cannot be prepared via metallation [e.g., the reaction of Au with  $\text{KC}_2\text{H}$  in liq  $\text{NH}_3$  gives<sup>8</sup>  $\text{K}[\text{Au}(\text{C}\equiv\text{CH})_2]$ , but they are synthesized via the reaction of freshly reduced  $\text{AuCl}_3$  with the corresponding alkynylsodium or -potassium. The resulting insoluble products are reacted further with donor ligands, such as amines, phosphines, or isocyanides, affording alkynylgold(I)-ligand complexes that have better solubility than the parent compounds<sup>9,10</sup>.

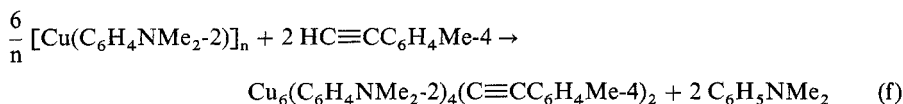
Metallation reactions are used for quantitatively converting a CH-acidic compound with methylcopper or phenylcopper into an organocopper complex:



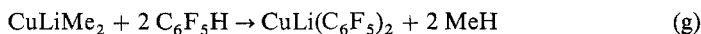
where  $\text{R} = \text{H}$ ,  $\text{CH}_3$ <sup>11</sup>,  $\text{CN}$ <sup>12</sup> and THF is tetrahydrofuran;



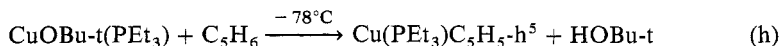
Insoluble  $\text{CuC}_6\text{H}_4\text{NMe}_2\text{-2}$  reacts with 4-tolylacetylene to give a soluble mixed-aryl-alkynylcopper species in 58 % yield<sup>15,16</sup>:



Also, diarylcuprate compounds,  $\text{CuLi}(\text{C}_6\text{F}_5)_2$ , can be prepared via metallation<sup>17</sup>:



Terminal acetylenes, cyclopentadiene (at  $-78^\circ\text{C}$ ), indene and other CH-acidic compounds can be metallated under extremely mild conditions by Cu(I) t-butoxide, e.g.<sup>17-19</sup>:



A less convenient route for the preparation of cyclopentadienylcopper-ligand complexes involves the use of Cu(I) oxide. Purification of the organocopper complexes is difficult because of the decomposition products formed by subsequent hydrolysis by  $\text{H}_2\text{O}$  produced in the metallation reaction, e.g.<sup>20,21</sup>:



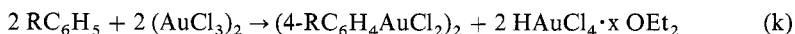
where  $\text{L} = \text{t-BuNC}$ ,  $\text{PEt}_3$ .

Metallation is rare in organogold chemistry. Low yields are obtained by direct auration of arenes<sup>22,23</sup>:



where R = H, Me, Ph.

Under somewhat different conditions auration proceeds via<sup>24</sup>:

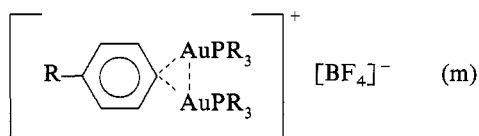
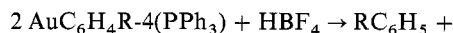


where R = H, Me, Et, i-Pr, t-Bu, Ph. The side products and the low yields make these reactions impracticable for monoarylgold(III) halides.

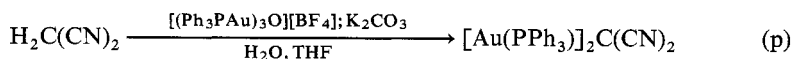
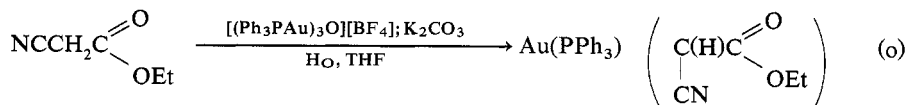
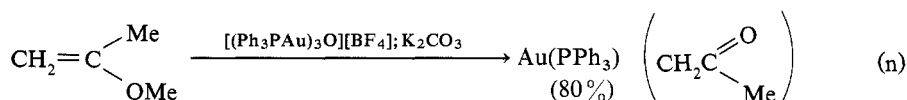
When R contains a coordinating group, single complexes instead of auration products form, e.g.<sup>23</sup>:



The 1 : 1 reaction of arylgold(I) complexes with  $\text{HBF}_4$  proceeds quantitatively<sup>26</sup>:

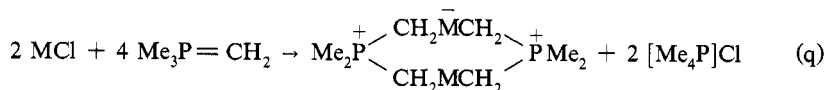


The auration reagent<sup>25</sup>,  $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{X}$ , shows versatile metallation reactivity; e.g., CH-acidic molecules, such as ferrocenes, aliphatic and aromatic ketones, enol ethers and esters, are aured under mild conditions, affording the corresponding organogold(I) compounds in excellent yields:

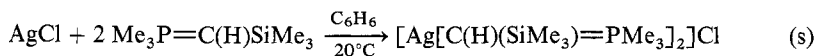
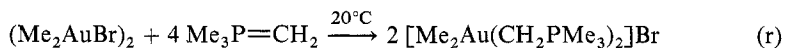


The presence of bases, e.g., sodium hydride or potassium carbonate is essential<sup>26</sup>.

Metal(II)-ylid complexes can be prepared for all three metals<sup>3,29,31</sup>, e.g.:



where M = Cu, Ag or Au(I). Metal-IB-ylid complexes are synthesized via direct coordination of the ylid to the IB-metal salt or compound<sup>3,29-33</sup>:



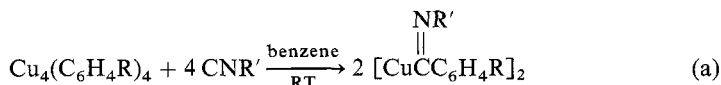
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5.6. Formation of Bonds between Elements of Groups IVB and IB 233  
 5.6.4. from the Metal Salts

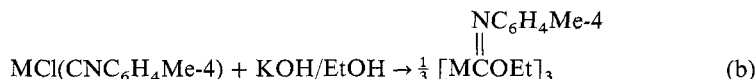
**5.6.4.4. by Insertion.**

Isonitriles insert into the Cu-C bond of arylcoppers. These reactions, which afford new Cu-carbon bonds, proceed quantitatively at RT<sup>1</sup>:



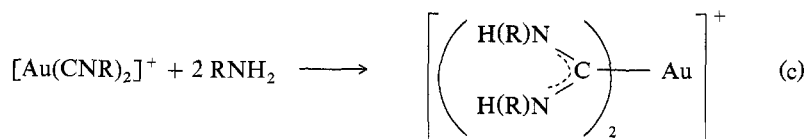
where R = CH<sub>2</sub>NMe<sub>2</sub>-2, NMe<sub>2</sub>-2, Me-2; R' = Me, t-Bu, c-Hex.

Similar insertion reactions into the Ag- or Au-C bond are not known. However, for these metals related products can be synthesized via addition<sup>2-4</sup>:

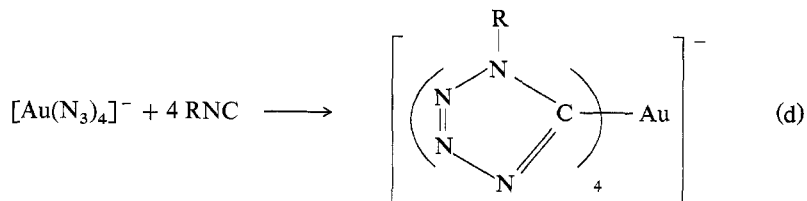


where M = Ag(I), Au(I).

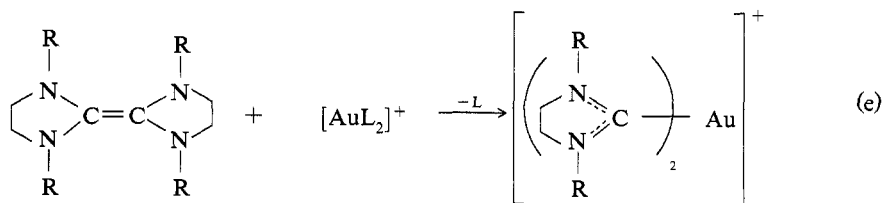
Other additions that form new Au-C bonds involve coordinated isocyanides<sup>5,6</sup>:



where R = Me as well as<sup>7</sup>:



Finally, Au(I)-carbene complexes can be prepared in excellent yields via<sup>8</sup>:



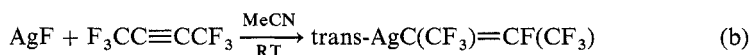
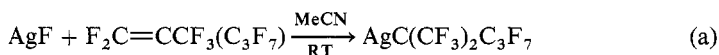
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5. L. Manojlarić-Muir, *J. Organomet. Chem.*, **73**, C45 (1974).
6. J. E. Parks, A. L. Balch, *J. Organomet. Chem.*, **71**, 453 (1974).
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8. B. Cetinkaya, P. Dixneuf, M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1827 (1974).

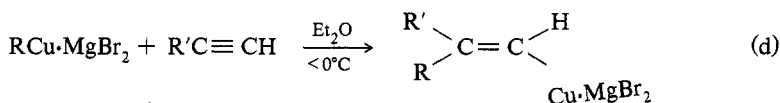
#### 5.6.4.5. by Addition, Decarboxylation.

A unique route is available for the synthesis of alkyl- and alkenylcopper and silver compounds. Addition reactions of AgF to alkenes<sup>1</sup>, alkynes<sup>2</sup> or allenes<sup>3</sup> proceed (in 50–70% yield) under mild conditions:



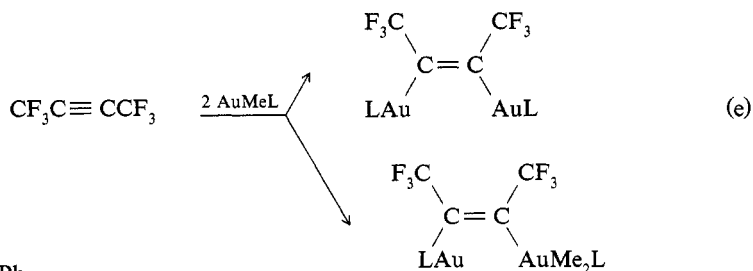
Alkylcopper reagents ( $\text{CuR-MgX}_2$ ,  $\text{CuR-LiX}$ ) add to acetylene or alkynes in a *cis* manner under mild conditions. This method generates alkenyl or alkylcopper intermediates, which subsequently are quenched in a second reaction with organic halides or other substrates<sup>4</sup>:

Pure organocoppers are not isolated:



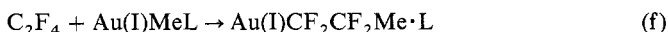
where R, R' = Et, n-Bu, Ph.

In organogold chemistry examples are known of synthetically useful additions; e.g.,  $\text{CF}_3\text{C}\equiv\text{CH}$  reacts with  $\text{Au(I)MeL}$  to  $\text{CF}_3\text{C}\equiv\text{CAuL}$  and with  $\text{Au(III)Me}_3\text{L}$  to *cis*- $\text{AuMe}_2\text{L}(\text{C}\equiv\text{CCF}_3)$ . However, with<sup>5</sup>  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ :



where L =  $\text{PPh}_3$ .

Moreover, alkylgold(I) compounds are formed<sup>6</sup>:

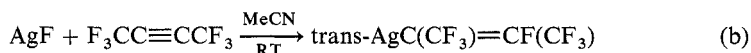
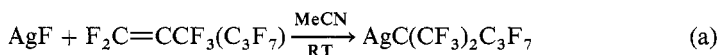


Examples of useful decarboxylations include the preparation of the quinoline complex of  $\text{CuC}_6\text{F}_5$  in good yield by heating to  $60^\circ\text{C}$   $\text{Cu(I)O}_2\text{CC}_6\text{F}_5$  in quinoline<sup>7</sup>.

5. L. Manojlarić-Muir, *J. Organomet. Chem.*, **73**, C45 (1974).
6. J. E. Parks, A. L. Balch, *J. Organomet. Chem.*, **71**, 453 (1974).
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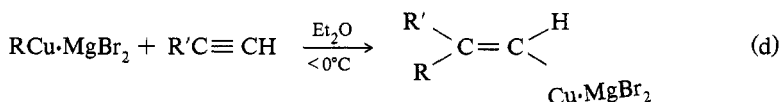
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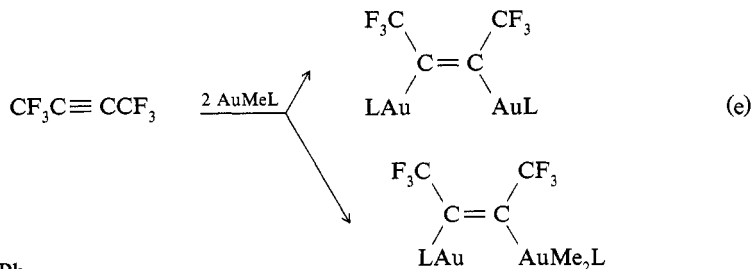
Alkylcopper reagents ( $\text{CuR-MgX}_2$ ,  $\text{CuR-LiX}$ ) add to acetylene or alkynes in a *cis* manner under mild conditions. This method generates alkenyl or alkylcopper intermediates, which subsequently are quenched in a second reaction with organic halides or other substrates<sup>4</sup>:

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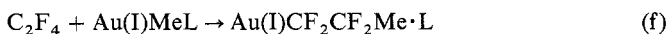
where R, R' = Et, n-Bu, Ph.

In organogold chemistry examples are known of synthetically useful additions; e.g.,  $\text{CF}_3\text{C}\equiv\text{CH}$  reacts with  $\text{Au(I)MeL}$  to  $\text{CF}_3\text{C}\equiv\text{CAuL}$  and with  $\text{Au(III)Me}_3\text{L}$  to *cis*- $\text{AuMe}_2\text{L}(\text{C}\equiv\text{CCF}_3)$ . However, with<sup>5</sup>  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ :



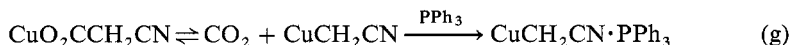
where L =  $\text{PPh}_3$ .

Moreover, alkylgold(I) compounds are formed<sup>6</sup>:

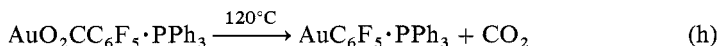


Examples of useful decarboxylations include the preparation of the quinoline complex of  $\text{CuC}_6\text{F}_5$  in good yield by heating to  $60^\circ\text{C}$   $\text{Cu(I)O}_2\text{CC}_6\text{F}_5$  in quinoline<sup>7</sup>.

Reversible decarboxylation is known<sup>8</sup> for  $\text{CuO}_2\text{CCH}_2\text{CN}$ :



An Au-C bond is formed in the decarboxylation reaction<sup>9</sup>:



Decarboxylation is of limited synthetic value because the forcing conditions contrast with the limited thermal stability of the metal IB-carbon bond.

(G. VAN KOTEN)

1. W. T. Miller, R. J. Burnard, *J. Am. Chem. Soc.*, **90**, 7367 (1968).
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4. J. F. Normant, in *New Applications of Organometallic Reagents in Organic Synthesis*, D. Seyferth, ed., Elsevier, Amsterdam, 1976, p. 219.
5. J. A. J. Jarvis, A. Johnson, R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 938 (1972); 373 (1973).
6. C. M. Mitchell, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 932 (1972), and refs. therein.
7. A. Cairncross, J. R. Roland, R. M. Henderson, W. A. Sheppard, *J. Am. Chem. Soc.*, **92**, 3187 (1970).
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#### 5.6.4.6. by Forming Adducts with Unsaturated Hydrocarbons.

Reviews of coordination of unsaturated and aromatic compounds with group-IB metal salts are cited in §5.6.2.3.

Copper(I) complexes are less stable than the corresponding Ag(I) and Au(I) complexes. They are prepared via the interaction of the unsaturated hydrocarbon with the cationic metal-IB center. Suitable starting materials are:

1.  $\text{Cu(II)(ClO}_4)_2$  and  $\text{Cu(BF}_4)_2$  both under reducing conditions, e.g.<sup>1</sup>, with Cu(0), benzene-soluble  $\text{CuO}_3\text{SCF}_3$ , Cu(I) halides in combination with  $\text{AlX}_3$  (formation of  $\text{AlX}_4^-$  anion and  $\text{Cu}^+$ ),
2.  $\text{AgBF}_4$ ,  $\text{AgNO}_3$ ,  $\text{AgO}_3\text{SCF}_3$ ,  $\text{AgO}_2\text{CCF}_3$ , or
3.  $\text{AuCl}_3$  (formation of  $[\text{AuCl}_4]^-$  anion and  $\text{Au}^+$ ).

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Unsaturated molecules that coordinate to cationic metal-IB centers include:

- (a) cyclic and acyclic olefins containing one or more  $\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$  units; (b) aromatic hydrocarbons, such as benzene and naphthalene; (c) alkynes containing one or more  $\text{—C}\equiv\text{C—}$  units, but not the terminal alkynes because of competing metallation reactions (see §5.6.2.3.3). In addition, each of these hydrocarbons may contain heteroatoms or groups.

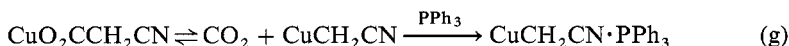
(G. VAN KOTEN)

1. R. G. Salomon, J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 3300 (1973).
2. F. M. Hartley, *Chem. Rev.*, 163 (1973); *J. Chem. Soc., Dalton Trans.*, 469 (1977).
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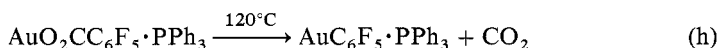


5.6. Formation of Bonds between Elements of Groups IVB and IB 235  
 5.6.4. from the Metal Salts

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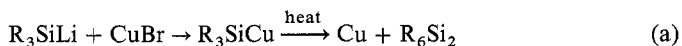
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3. C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, J. G. Noltes, *Organomet. Chem. Rev.*, **A**, **5**, 215 (1970).

## 5.6.5. From the Metal–Phosphine Complexes

### 5.6.5.1. with Triaryl Group IV–Alkali-Metal Derivatives.

Treatment of  $\text{Ph}_3\text{PAuCl}$  with triphenysilyllithium in tetrahydrofuran (THF) gives  $\text{Ph}_3\text{PAuSiPh}_3$  as a tan solid which is both air and light sensitive, in contrast to the Ge analogue<sup>1</sup>. The analogous reaction in the absence of a coordinating phosphine produces a polymeric solid,  $\text{R}_3\text{MCu}$ , that on heating decomposes<sup>2</sup> to  $\text{Cu}(0)$ :



Copper-, Ag- and Au–Ge complexes are prepared with the group-IB metal in its +1 oxidation state. The thermal stability and reactivity depend on surrounding both metals with relatively bulky groups, and pure Cu and Ag complexes are isolated only with the metal tetracoordinated<sup>3</sup>.

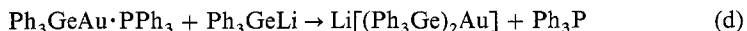
Triphenylgermyllithium (from  $\text{Ph}_6\text{Ge}_2$  or  $\text{Ph}_4\text{Ge}$  and Li) in 1,2-dimethoxyethane (DME) reacts with  $(\text{Ph}_3\text{PCuI})_4$  to give an insoluble, thermally unstable complex of unknown composition, which fumes on exposure to air. However, if xs triphenylphosphine is used, then the monomeric complex  $\text{Ph}_3\text{GeCu}(\text{PPh}_3)_3$  may be isolated in low yield from benzene.

Triphenylphosphinesilver iodide,  $[\text{Ph}_3\text{PAgI}]_4$ , behaves in a similar way with  $\text{Ph}_3\text{-GeLi}$ , yielding a brown, insoluble powder that decomposes rapidly to Ag metal on exposure to air. When this material is treated with xs  $\text{Ph}_3\text{P}$  (or if the original reaction is carried out with free  $\text{Ph}_3\text{P}$  present), then pale-green crystals of  $\text{Ph}_3\text{GeAg}(\text{PPh}_3)_3$  are isolated. The corresponding complex,  $\text{Ph}_3\text{GeAg}(\text{PET}_2\text{Ph})_3$ , is unstable. Unlike Cu and Ag, Au forms two-coordinated complexes in its +1 oxidation state. Triphenylphosphine-gold chloride reacts with  $\text{Ph}_3\text{GeLi}$  to give an air- and water-stable crystalline complex:

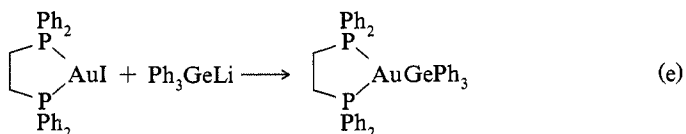


Changing the donor-acceptor and steric properties of the phosphine, as in  $\text{Me}_3\text{PAuI}$ , results in a complex of lower stability, viz.,  $\text{Me}_3\text{PAuGePh}_3$ .

An anionic Ge–Au complex forms as a white, insoluble complex of low thermal stability when  $\text{Ph}_3\text{GeAuPPh}_3$  is treated with phenyllithium in ether:



This complex is stable in the form of its tetraethylammonium salt. The coordination number of Au can be raised to three as in:



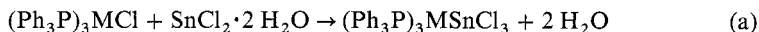
(F. GLOCKLING)

1. M. C. Baird, *J. Inorg. Nucl. Chem.*, **29**, 367 (1967).
2. E. H. Brooks, R. J. Cross, *Organomet. Chem. Rev.*, **A6**, 227 (1970).
3. F. Glockling, K. A. Hooton, *J. Chem. Soc.*, 2658 (1962).

5.6. Formation of Bonds between Elements of Groups IVB and IB 237  
 5.6.5. from the Metal-Phosphine Complexes

**5.6.5.2. by Insertion.**

Compounds containing Sn—Cu, Sn—Ag and Sn—Au bonds are prepared by inserting SnCl<sub>2</sub> into the transition metal–halogen bond:



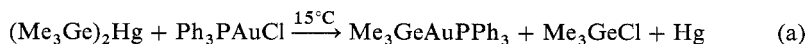
Unlike many metal–metal bond formations, these reactions occur in H<sub>2</sub>O giving complexes with sharp mp's in high yield. Low-temperature <sup>31</sup>P NMR spectra of (Ph<sub>3</sub>P)<sub>3</sub>–AgSnCl<sub>3</sub> give evidence for both the covalent and ionic, [(Ph<sub>3</sub>P)<sub>3</sub>Ag]<sup>+</sup>[SnCl<sub>3</sub>]<sup>–</sup>, forms<sup>1</sup>. The gold complex, (Ph<sub>3</sub>P)<sub>3</sub>AuSnCl<sub>3</sub>, is four coordinated, like those<sup>2</sup> of Cu and Ag, although 1 mol of Ph<sub>3</sub>P is removed by extraction with hexane. The Au–Sn clusters (Ph<sub>3</sub>P)<sub>4</sub>Au<sub>4</sub>SnCl<sub>3</sub> and (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>SnI<sub>2</sub> are of unknown structure<sup>3</sup>.

(F. GLOCKLING)

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**5.6.5.3. by Transmetallation.**

When bis(trimethylgermyl)mercury is refluxed with Ph<sub>3</sub>PAuCl decomposition occurs, but at low T the stable Ge–Au complex can be isolated in 16% yield:



This reaction can be applied to many transition-metal complexes either with or without change in the oxidation state of the transition metal.

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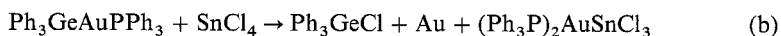
1. F. Glockling, M. D. Wilby, *J. Chem. Soc.*, 2168 (1968).

**5.6.5.4. by Metal–Halide Exchange.**

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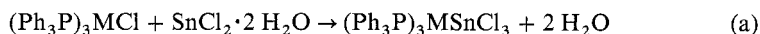
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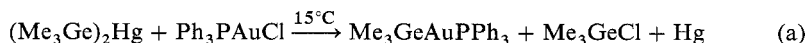
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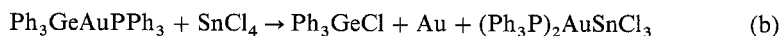
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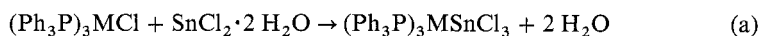
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5.6. Formation of Bonds between Elements of Groups IVB and IB 237  
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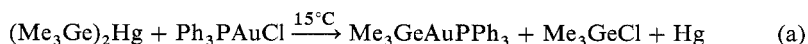
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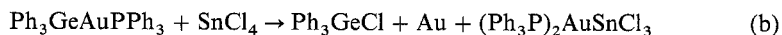
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## 5.7. Formation of Bonds between Elements of Group IVB (C, Si, Ge, Sn, Pb) and Group IIB (Zn, Cd, Hg)

### 5.7.1. Introduction

In this chapter are found the reactions used to prepare the Zn, Cd and Hg derivatives of the main fourth-group elements. Because of the great usefulness of the organo-Zn and -Hg reagents in synthesis, the formation of the bond between carbon and the group-IIB elements is singled out for separate treatment. After discussing the preparation of these compounds from the group-IIB metals, their alloys and salts and from other groups-IIB organometallics by exchange, the formation of the silyl-, germyl-, stannyl- and plumbyl-derivatives is considered.

(J. J. ZUCKERMAN, ED.)

### 5.7.2. Carbon–Group-IIB Bonds

#### 5.7.2.1. from the Elements.

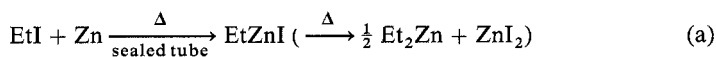
The metals of group IIB do not form carbides.

(E. K. STORMS)

#### 5.7.2.2. from the Group-IIB Metals and Alloys

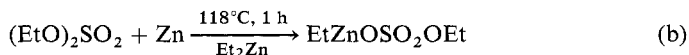
##### 5.7.2.2.1. with Organic Halides and Sulfates<sup>1,2</sup>.

(i) Zinc. Zinc metal can react directly with alkyl iodide, RI, in the absence of solvents at elevated T to yield organozinc species<sup>3</sup>:

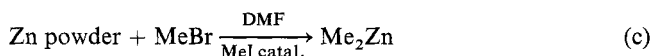


At the T used for these reactions, disproportionation of the first-formed products, RZnI, to R<sub>2</sub>Zn and ZnI<sub>2</sub> may result, but at lower T, e.g., 85–90°C with EtI and Zn dust, the organozinc iodides can be isolated<sup>4</sup>. As R<sub>2</sub>Zn compounds can inflame in air, an inert atmosphere, e.g., CO<sub>2</sub>, should be provided. Dialkyl sulfates also react with Zn metal with

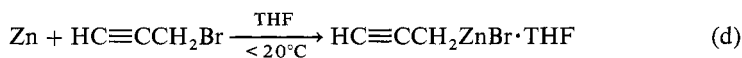
$R_2Zn$  or  $RI$  as catalysts, e.g.<sup>5</sup>:



Reactions also may be carried out in coordinating solvents, such as  $N,N$ -dimethylformamide (DMF), 1,2-dimethoxyethane (DME), diglyme or dimethylsulfoxide (DMSO) or in high-bp nonpolar solvents. Reactions in polar solvents proceed not only with alkyl iodides and diiodides<sup>6</sup>, but also with the lower alkyl bromides<sup>7</sup>. For these bromides some heating may be necessary to initiate the reaction; alternatively, the corresponding alkyl iodide can be used as catalyst<sup>8</sup>:

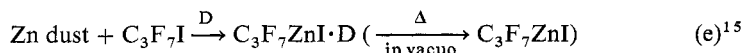


As well as the simple alkyl iodides and bromides, other organic halides react directly with  $Zn$  metal in polar solvents, e.g., (i) triphenylmethyl chloride<sup>9</sup> in DMF, (ii) propargylic bromides<sup>10,11</sup> in tetrahydrofuran (THF), e.g.:



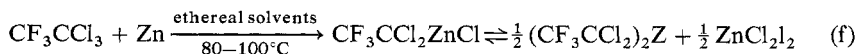
(iii) allylic bromides in THF<sup>12,13</sup> (without producing diallyl compounds), (iv) perhaloalkanes<sup>14-16</sup> and -arenes<sup>17</sup> and (v) bromoalkanes, containing such substituents as  $CN$ ,  $CONR_2$  and  $CO_2R$ .

The reactions of perfluoroalkyl halides with  $Zn$  dust proceed in coordinating polar solvents such as 1,4-dioxane or DMF, e.g.:



(where  $D$  = solvent: dioxane,  $Et_2O$ ,  $n\text{-Bu}_2O$  or THF) in contrast<sup>14,15</sup> to reactions in the absence of such solvents; e.g., no reaction occurs on heating  $C_5F_{11}I$  with  $Zn$  dust in benzene or in the absence of a solvent to  $100^\circ C$ . The product from  $C_3F_7I$  and  $Zn$  metal on strong heating (to  $310^\circ C$ ), in the absence of a solvent is not an organozinc<sup>14</sup>, but the coupled dimer,  $C_3F_7 \cdot C_3F_7$ . Other products from reactions of  $R_FI$  with metallic  $Zn$ , even in polar solvents, are perfluoroalkenes,  $R_FH$ , and polyfluoroalkanes,  $R_FH$ , and hence can limit the utility of the reactions. Formation of  $CF_3H$  and  $CF_3CF_2H$  predominates in the reaction of  $CF_3I$  and  $CF_3CF_2I$  with  $Zn$  metal in coordinating solvents; no organozincs are detected. As shown in Eq. (e), the coordinated solvent molecule can be removed by heating in vacuo.

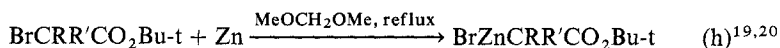
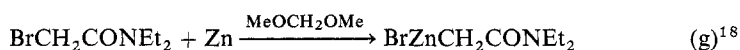
As well as the perfluoroalkyl halides, some fluoroalkyl chlorides, e.g.<sup>16</sup>,  $CF_3CCl_3$ :



and perfluoroalkyl bromides, e.g.<sup>14,15</sup>,  $C_3F_7Br$ , provide organozinc species with  $Zn$  metal in polar solvents.

Pentafluorophenyl bromide or iodide reacts with  $Zn$  wool to give<sup>17</sup>  $C_6F_5ZnX$  ( $X = Br$  or  $I$ ) quantitatively in THF,  $Et_2O$ , DME, glyme, DMF, DMA or DMSO.

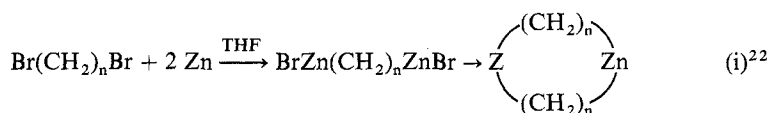
Substituted alkyl bromides ( $\text{RR}'\text{CBrX}$ ,  $\text{X} = \text{CN}$ ,  $\text{CO}_2\text{R}$  or  $\text{CONR}_2$ ) react with Zn metal in ethers<sup>18-20</sup>:



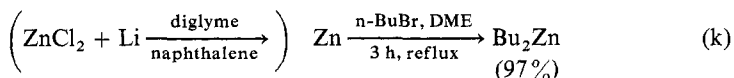
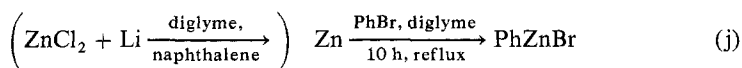
Such organozincs also are formed as transient species in the reaction of a Zn derivative of an  $\alpha$ -bromoester with an aldehyde or ketone<sup>21</sup>, viz., involving Zn, carbonyl compounds and substituted alkyl bromides.

Zinc powder, dust, wool, turnings or granules may not be sufficiently reactive; finely divided samples, or alloys or couples are more potent forms of Zn.

Particularly reactive forms of Zn metal are produced by reduction of Zn halides by alkali metals (Li, Na or K). These reductions lead to finely divided Zn. Such forms of Zn metal react with  $\alpha,\omega$ -dibromoalkanes:



where  $n = 4-6$ . The Li-ZnCl<sub>2</sub>-naphthalene combination produces a reactive Zn metal, and one that reacts with PhBr in refluxing diglyme and with n-BuBr in refluxing DME:



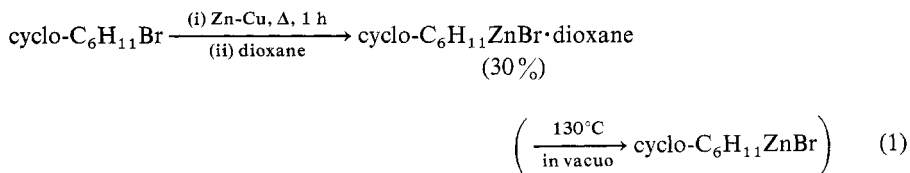
to react with  $\text{Br}_2\text{CHMe}$ , and takes part in reactions with  $\text{ClCH}_2\text{CO}_2\text{Et}$ <sup>23</sup>. A finely divided Zn slurry is obtained by cocondensing Zn vapor and a solvent at 77 K. On warming to RT, these Zn slurries react with RBr (e.g.,  $\text{R} = \text{Me}$ , Et, n-Pr, n-Bu or  $\text{CH}_2\text{Br}$ ) not only in coordinating solvents, such as THF, dioxane or DME (glyme), but also in hydrocarbons, e.g., toluene or hexane. By using the reactive Zn slurry in hexane, a pure sample of  $\text{R}_2\text{Zn}$ , e.g.,  $\text{R} = \text{Me}$ , can be achieved on simple distillation from the reaction mixture<sup>24,25</sup>. The cocondensation of Zn atoms and  $\text{R}_\text{F}\text{I}$  on warming provides unsolvated  $\text{R}_\text{F}\text{ZnI}$  having a greater reactivity and a reduced thermal stability compared to the solvated samples formed by the more usual reactions of Zn metal and perfluoroalkyl iodides in coordinating solvents<sup>26</sup>.

Combinations of Zn and other metals are used with Zn-Cu couples being the most popular<sup>27-34</sup>. Recipes for their preparation<sup>2</sup> involve, e.g., Zn dust and Cu(II) salts, such as citrate<sup>29</sup> or acetate<sup>27</sup>, as well as treatment of Zn and Cu powders at 400°C under  $\text{H}_2$ <sup>32</sup>.

One Zn-Cu couple<sup>27</sup>, made from Zn dust and  $\text{Cu}(\text{OAc})_2$  in glacial acetic acid, reacts on heating with RBr ( $\text{R} = \text{cyclo-C}_6\text{H}_{11}$ , t-Bu or n-C<sub>7</sub>H<sub>15</sub>). Addition of dioxane to the



mixture allows isolation of  $RZnBr$  as its dioxane complex:



The gem-dibromide,  $\text{Me}_3\text{SiCHBr}_2$ , reacts<sup>31</sup> with a Zn–Cu couple in THF at  $60^\circ\text{C}$  to give the gem-bis(bromo)zinc compound,  $\text{Me}_3\text{SiCH}(\text{ZnBr})_2$ .

Alkyl iodides<sup>27,28,30</sup> and perfluoroalkyl iodides<sup>29</sup> react with Zn–Cu couples. Use also is made of mixtures of the alkyl iodide and bromide<sup>28</sup> (e.g., a 1:3 ratio of  $n\text{-BuI} : n\text{-BuBr}$  gives  $n\text{-Bu}_2\text{Zn}$  in high yield). Byproducts, such as alkenes ( $R\text{—H}$ ) and alkanes,  $\text{RH}$ , can become problems for secondary alkyl halides,  $\text{RX}$ , and for these care and control of the conditions and workup are vital. Success is possible as shown<sup>33</sup> by yields of 85% for  $i\text{-Pr}_2\text{Zn}$ , and 72% for  $s\text{-Bu}_2\text{Zn}$ . Tertiary alkyl iodides do not produce organozincs.

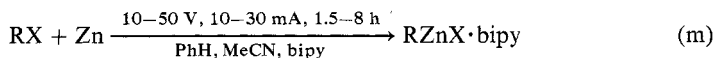
Organozincs free of complexing solvents may be produced using Zn–Cu couples in a mixed hydrocarbon–carbonyl medium, e.g.,  $\text{MeCO}_2\text{Et}$ , or  $\text{MeCO}_2\text{Me}$ . For primary alkyl iodides, benzene or toluene is recommended, but for secondary compounds, a nonaromatic hydrocarbon is preferred<sup>1</sup>.

Zinc–copper couples are used in reactions of a Zn derivative of an  $\alpha$ -bromoester with an aldehyde or ketone, or even with  $\alpha$ -chloroalkyl esters<sup>34</sup>, and in reactions of  $\text{CH}_2\text{I}_2$  and Zn in cyclopropane formation from alkenes,  $\text{CH}_2\text{I}_2$  and Zn. In the  $\text{CH}_2\text{I}_2$ –Zn–Cu reactions the organozinc trapped by  $\text{Me}_3\text{SnX}$  is  $\text{IZnCH}_2\text{I}$ , whereas in the  $\text{CH}_2\text{I}_2$ –Zn dust– $\text{Me}_3\text{Al}$  reaction the trapped species<sup>35</sup> is  $(\text{IZn})_2\text{CH}_2$ .

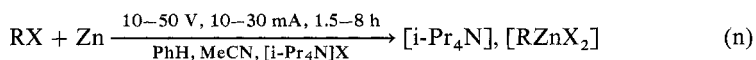
In addition to Zn–Cu couples, Zn dust– $\text{Cu}_2\text{Cl}_2$  combinations are also employed<sup>36</sup>.

Other Zn metal combinations include Zn–Na, Zn–Mg alloys, and Zn–Li, Zn–Ag couples and amalgams. A Zn–Ag couple, made from  $\text{MeCO}_2\text{Ag}$  and Zn metal in acetic acid, is used<sup>37</sup> with  $\text{CH}_2\text{I}_2$ .

Electrochemical synthesis<sup>38,39</sup> of neutral and anionic organozincs is also realized from an organic halide, a Zn electrode and an electrolyte of  $\text{MeCN}$  and  $\text{PhH}$ :



where  $R = \text{Me, Et, CF}_3, \text{CH}_2=\text{CH, Ph, C}_6\text{F}_5$  or  $\text{PhCH}_2$  and  $X = \text{Cl, Br or I}$ ;



where  $R = \text{Me, Et, Ph or CF}_3$  and  $X = \text{Cl, Br or I}$ .

Ultrasound accelerates formation of organozincs<sup>40</sup>.

(ii) Cadmium. Organocadmiums are seldom made from Cd metal and organic halides, but  $\text{RI}$  ( $R = \text{Et, i-Pr, Bu, allyl, propargyl or benzyl}$ ) reacts with Cd in hexamethylphosphoramide (HMPA), DMF or DMSO to give  $\text{R}_2\text{Cd} \cdot \text{HMPA}$ <sup>44</sup>.

Pentafluorophenyl iodide,  $C_6F_5I$ , and  $\alpha$ -bromoacetates react with Cd turnings in polar solvents, e.g.<sup>45</sup>:



Cadmium metal also reacts<sup>46</sup> with  $(EtO)_2P(O)CF_2Br$  to give  $[(EtO)_2P(O)CF_2]_2Cd$  and  $(EtO)_2P(O)CF_2CdBr$ .

Reactive forms of Cd metal are obtained from  $Li[C_8H_{10}]^-$  reductions of  $CdCl_2$  and also Cd-Li alloys; these react with alkyl bromides, aryl iodides and benzyl chlorides<sup>47</sup>.

Cadmium slurries, formed from codeposition of Cd vapor with a solvent at 77 K followed by warming to RT, are sufficiently reactive toward RI in hexane, toluene, THF, dioxane or diglyme<sup>23</sup>. Reactions do not proceed well with RBr; e.g., only a 10% yield of propylcadmiums is obtained on refluxing in diglyme overnight. The presence of KI increases the reactivity of the slurries. Ethyl iodide reacts at  $-196^\circ C$  with a Cd slurry, obtained from simultaneous evaporation of PhMe and Cd in a metal-atom reactor<sup>48</sup>; the yield of nonvolatile  $EtCdI$  is 55%.

Electrochemical synthesis is also successful with Cd electrodes, a low voltage and an  $RX-MeOH$  electrolyte medium. These syntheses form unsolvated  $RCdX$  or the more stable complexes.  $RCdX \cdot D$  ( $RX = MeI, EtBr, EtI, n-BuCl, PhBr$  or  $C_6F_5Br$ ;  $D =$  bipy, DMSO, 1,10-phen or 1,4-dioxane) if a donor,  $D$ , is also present<sup>39,49,50</sup>. Anionic complexes,  $[R'_4N][RCdX_2]$ , also are formed if  $[R'_4N]X$  is added to the electrolytic medium ( $R =$  alkyl, perfluoroalkyl, aryl or  $C_6F_5$ ;  $X = Cl, Br$  or  $I$ )<sup>51</sup>.

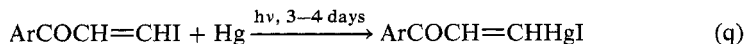
(iii) Mercury. Simple alkyl iodides (e.g.,  $R = Me, PhCH_2$  or  $ICH_2$ ) react with Hg metal in sunlight or upon UV-irradiation<sup>52</sup>:



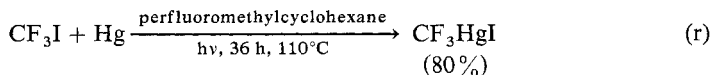
Mercury(I) iodide also catalyzes the reaction of  $MeI$ <sup>52</sup>. For the more reactive allylic iodide and cinnamyl bromide, irradiation is not necessary<sup>53</sup>.

Simple alkyl bromides or chlorides do not react with Hg on irradiation, and only low yields of  $ArHgI$  are obtained from aryl iodides<sup>53</sup>. Diiodomethane reacts with Hg metal on irradiation in PhH to give both  $IHgCH_2I$  and  $CH_2(HgI)_2$ <sup>54</sup>.

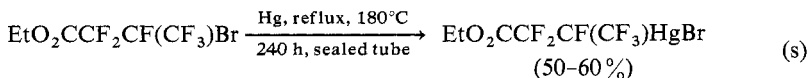
Other organic halides reactive toward Hg metal are propargyl bromides and iodide<sup>55</sup> and acylvinyl iodides<sup>56</sup>:



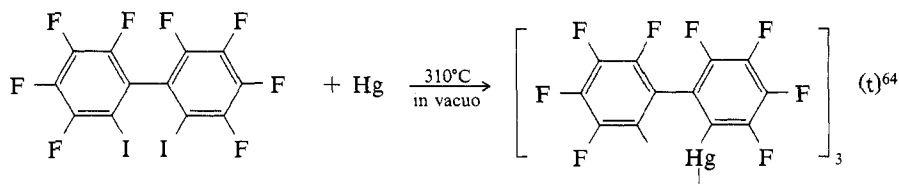
Trifluoromethyl iodide reacts<sup>57</sup> with Hg metal on heating and irradiation (sunlight or UV-lamp) in solution:



In the absence of a solvent conditions required for reaction are more severe, i.e.,  $260-290^\circ C$  for 12 h without irradiation or  $150^\circ C$  with UV irradiation<sup>57</sup>. Trichloromethyl bromide in the presence of 2,2-azobisisobutyronitrile (AIBN)<sup>58</sup>, and trichloromethyl iodide and UV-irradiation<sup>59</sup>, provides  $Cl_3CHgX$  derivatives on heating with Hg metal at  $70-80^\circ C$ . Perfluoroalkylbromides also react<sup>60</sup>:

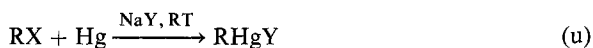


Reactions of  $C_6H_5CH_2Br$  ( $X = Cl, Br$ ) with Hg metal proceed on UV irradiation<sup>61</sup>. Perfluoroaryl iodides can undergo thermal reactions with Hg<sup>62–64</sup>; e.g.,  $C_6F_5I$  and Hg at 300°C for 30 h provide<sup>62</sup>  $(C_6F_5)_2Hg$  (75 % yield) and  $HgI_2$ :



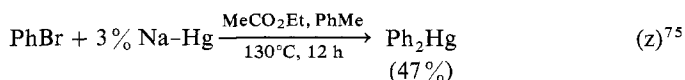
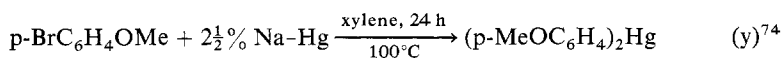
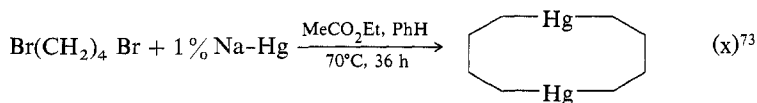
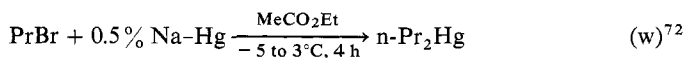
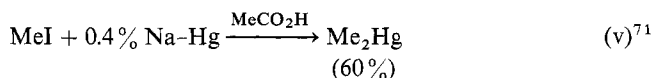
Compounds  $YC_6H_4CHXCO_2R$  ( $X = Br$  or  $I$ ) also react<sup>65,66</sup> with Hg metal without heating or irradiation to give  $YC_6H_4CH(HgX)CO_2R$ ; ( $Y = F, Br, I, MeO, t\text{-Bu}, Me$  or  $NO_2$ ).

Reactions between organic halides and Hg metal proceed well in the presence of certain Na salts, NaY. The effectiveness of the anions decreases  $Y = I^- > [S_2O_3]^{2-} > [SCN]^- > Br^- > Cl^-$ . The best solvents are DME or diglyme<sup>67,68</sup>:

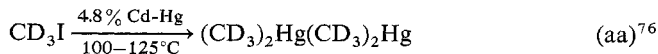


where  $RX = n\text{-BuI}, s\text{-BuBr}, PhCH_2Br, PhI$  or  $p\text{-O}_2NC_6H_4Br$  and  $Y = I^-, [S_2O_3]^{2-}, [SCN]^-, Br^-$ .

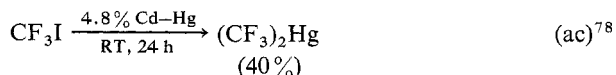
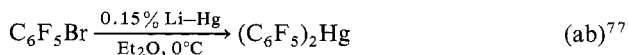
(iv) Amalgams. Amalgams are more reactive<sup>69,70</sup> than Hg metal alone, and use is made of Na amalgam in reactions with alkyl iodides and bromides (but not with chlorides) in the cold. Reactions with aryl iodides and bromides occur on heating and usually an amalgam with a higher Na content is taken. The products are most often the diorganomercurials. Catalysts, such as  $MeCO_2Me$  or  $MeCO_2Et$ , are also employed with primary alkyl ( $Me \rightarrow C_8H_{17}$ ), secondary alkyl (e.g.,  $i\text{-Pr}$  or  $cyclo\text{-}C_6H_{11}$ ) and aryl halides,  $ArX$  ( $Ar = Ph, \text{alkylphenyl}, p\text{-MeOC}_6H_4, p\text{-Me}_2NC_6H_4, \text{naphthyl, etc.}$ ), e.g.:



Other amalgams used include those of the other alkali metals, Cd, Cu and Ag, e.g.:

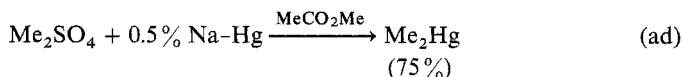


Amalgams react with perfluoroorganic halides:

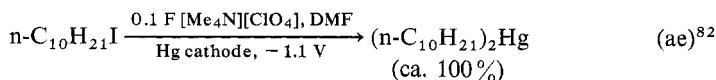


o-Phenylene- and o-terphenylenemercury are obtained from o-dibromobenzene and alkali-metal amalgams<sup>79-81</sup>.

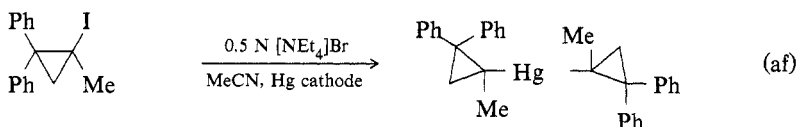
Dialkylsulfates also react with Na amalgams<sup>70</sup>:



(v) Electrochemical Synthesis<sup>83</sup>. These are used more frequently for organomercury than for either Zn or Cd. Among the organic halides that can take part in electrochemical synthesis with Hg cathodes are (a)<sup>83,84</sup> simple alkyl iodides, RI (e.g., R = Et, t-Bu, n-C<sub>10</sub>H<sub>21</sub>):

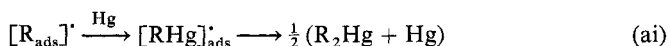


(b)<sup>85</sup> allylic bromide, (c)<sup>86,87</sup> benzylic iodides and bromides, (d)<sup>88</sup> cyclopropyl iodide:



(e)<sup>89</sup> BrCH<sub>2</sub>CH<sub>2</sub>CN, (f)<sup>90</sup> C<sub>6</sub>F<sub>5</sub>I and (g)<sup>91</sup> o-dihalobenzenes (which provide o-phenylenemercury).

The free-radical mechanism for formation of (n-C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>Hg depends on the potential, electrolysis time and H<sub>2</sub>O concentration. At potentials more positive than the polarographic maximum, the mechanism is<sup>92</sup>:



As in other electroreductions, the potential is most important with high applied potentials leading to low yields of diorganomercurials; e.g., in contrast to the 100% yield in Eq. (ae) at a potential of -1.1 V, the yield of (n-C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>Hg obtained at -1.9 V is 0%.

Only low yields of (1-norbornyl)<sub>2</sub>Hg are obtained from controlled-potential electrolysis of 1-iodo- and 1-bromonorbornane at Hg-pool electrodes in DMF containing [R<sub>4</sub>N][ClO<sub>4</sub>] as current carrier, the major product being norbornane<sup>93</sup>. The 1-halonorbornane reductions are two-electron processes, whereas only one electron is transferred in 1-halodecane reductions. The intermediate 1-norbornyl radical is reduced electrolytically (or accepts a hydrogen atom from the solvent), whereas the 1-decyl radical is absorbed onto Hg. The electrochemical reaction of I(CF<sub>2</sub>)<sub>4</sub>I in DMF provides<sup>94</sup> [H(CF<sub>2</sub>)<sub>4</sub>]<sub>2</sub>Hg via the intermediacy of I(CF<sub>2</sub>)<sub>4</sub>H and H(CF<sub>2</sub>)<sub>4</sub>HgI. The compounds [CH<sub>3</sub>(CH<sub>2</sub>)<sub>n-1</sub>]<sub>2</sub>Hg; n = 4-7 or 12, are obtained from the controlled-potential<sup>95</sup> electroreduction of Br(CH<sub>2</sub>)<sub>n</sub>Br.

(J. L. WARDELL)

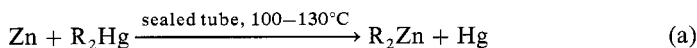
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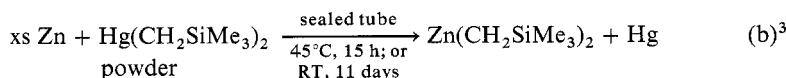
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#### 5.7.2.2.2. with Organomercurials.

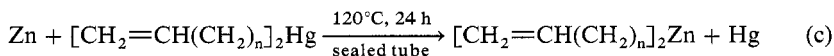
(i) Zinc. Reactions of Zn metal with diorganomercurials can produce diorgano-zincs.<sup>1-3</sup>:



where R = Me, Et, i-Pr, s-Bu or PhSCH<sub>2</sub>;

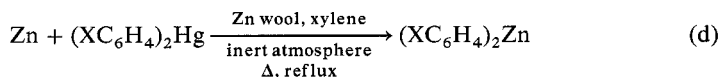


Dialkenylmercurials also take part<sup>4</sup>:

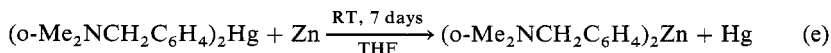


where n = 2, 3 or 4. With (5-hexenyl)<sub>2</sub>Hg, some cyclopentylmethylzincs (ca. 10%) are produced also.

Diarylzincs are prepared similarly<sup>5-7</sup> using Ar<sub>2</sub>Hg and either Zn filings<sup>5,6</sup> in a stream of dry H<sub>2</sub> or <sup>7</sup>Zn wool in xylene with an inert atmosphere, such as CO<sub>2</sub>:



where X = H, Cl, F or Me<sub>2</sub>N. Not all substituted arylmercurials react; e.g., p-bromo- and p-iodophenylmercurials do not participate. Powdered Zn is used also<sup>8</sup>:



Benzyl groups are not transferred from dibenzylmercury to Zn on heating; instead, dibenzyl is obtained.

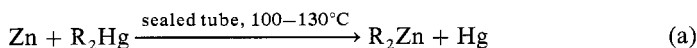
(ii) Cadmium. Cadmium is chemically too similar to Hg for the metal exchange to be useful for preparative purposes; instead, equilibria are established; e.g., heating Cd metal

5.7. Formation of Bonds between Elements of Groups IVB and IIB 247  
 5.7.2. Carbon-Group-IIB Bonds  
 5.7.2.2. from the Group-IIB Metals and Alloys

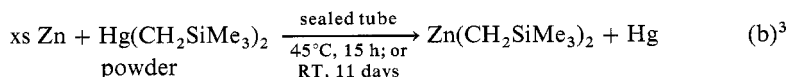
83. D. M. La Perriere, W. F. Carroll, B. C. Willett, E. C. Torp, D. G. Peters, *J. Am. Chem. Soc.*, **101**, 7561 (1979).
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94. P. Calas, P. Moreau, A. Commeyras, *J. Fluorine Chem.*, **12**, 67 (1978).
95. J. Casanova, H. R. Rogers, *J. Am. Chem. Soc.*, **96**, 1942 (1974).

**5.7.2.2.2. with Organomercurials.**

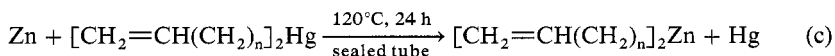
(i) Zinc. Reactions of Zn metal with diorganomercurials can produce diorganozincs.<sup>1-3</sup>:



where R = Me, Et, i-Pr, s-Bu or PhSCH<sub>2</sub>;

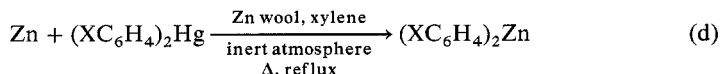


Dialkenylmercurials also take part<sup>4</sup>:

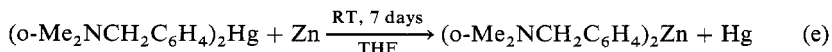


where n = 2, 3 or 4. With (5-hexenyl)<sub>2</sub>Hg, some cyclopentylmethylzincs (ca. 10%) are produced also.

Diarylzincs are prepared similarly<sup>5-7</sup> using Ar<sub>2</sub>Hg and either Zn filings<sup>5,6</sup> in a stream of dry H<sub>2</sub> or <sup>7</sup> Zn wool in xylene with an inert atmosphere, such as CO<sub>2</sub>:



where X = H, Cl, F or Me<sub>2</sub>N. Not all substituted arylmercurials react; e.g., p-bromo- and p-iodophenylmercurials do not participate. Powdered Zn is used also<sup>8</sup>:

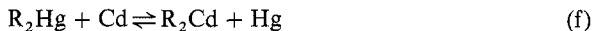


Benzyl groups are not transferred from dibenzylmercury to Zn on heating; instead, dibenzyl is obtained.

(ii) Cadmium. Cadmium is chemically too similar to Hg for the metal exchange to be useful for preparative purposes; instead, equilibria are established; e.g., heating Cd metal



with  $\text{Ph}_2\text{Hg}$  provides 3 : 1  $\text{Ph}_2\text{Cd}$  and  $\text{Ph}_2\text{Hg}$ :

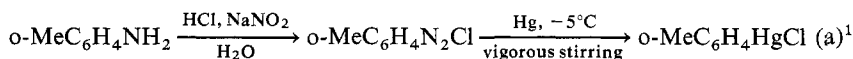


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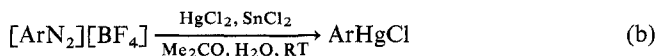
1. R. Taube, D. Steinborn, B. A. Adler, *J. Organomet. Chem.*, 275, 1 (1984).
2. C. R. McCoy, A. L. Allred, *J. Am. Chem. Soc.*, 84, 912 (1962).
3. D. M. Heinekey, S. R. Stobart, *Inorg. Chem.*, 12, 1463 (1978).
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9. S. Hilbert, G. Grüttner, *Chem. Ber.*, 46, 1682 (1913).

### 5.7.2.2.3. with Aryldiazonium Salts.

Arenediazonium salts,  $\text{ArN}_2\text{X}$ , react with Hg metal in aq acid<sup>1</sup> or in acetone<sup>2</sup> to give  $\text{ArHgX}$ :



Vigorous stirring by specially designed stirrers is essential for good yields. Finely divided Hg, formed<sup>3,4</sup> in situ from  $\text{HgCl}_2$  and  $\text{SnCl}_2$ , is used also:



Functional substituents, including halo, carbonyl or hydroxyl, are tolerated.

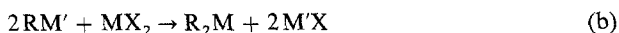
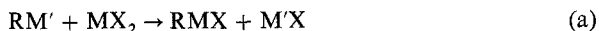
(J. L. WARDELL)

1. R. McClure, A. Lowry, *J. Am. Chem. Soc.*, 53, 319 (1931).
2. W. Waters, *J. Chem. Soc.*, 2007 (1937).
3. M. F. W. Dunker, E. B. Starkey, G. L. Jenkins, *J. Am. Chem. Soc.*, 58, 2308 (1936).
4. M. F. W. Dunker, E. B. Starkey, *J. Am. Chem. Soc.*, 61, 3005 (1939).

### 5.7.2.3. from Metal Salts

#### 5.7.2.3.1. with Organometallics.

Interactions of Zn, Cd or Hg salts ( $\text{MX}_2$ ) with organic derivatives of other metals ( $\text{RM}'$ ) can lead to mono- or dialkyl compounds<sup>1,2</sup>:



The metal(II) halides (chloride, bromide or iodide), carboxylates, and other salts find use, including  $\text{Hg(II)}$  fulminate<sup>3</sup>:

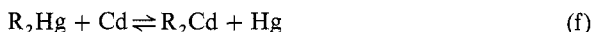


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### 5.7. Formation of Bonds between Elements of Groups IVB and IIB

#### 5.7.2. Carbon–Group-IIB Bonds

with  $\text{Ph}_2\text{Hg}$  provides 3 : 1  $\text{Ph}_2\text{Cd}$  and  $\text{Ph}_2\text{Hg}$ :

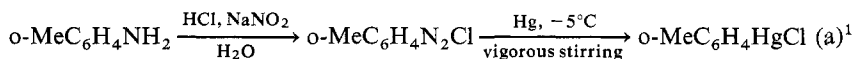


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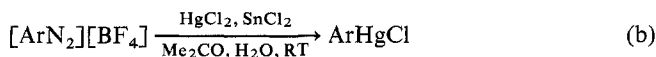
1. R. Taube, D. Steinborn, B. A. Adler, *J. Organomet. Chem.*, **275**, 1 (1984).
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9. S. Hilbert, G. Grüttner, *Chem. Ber.*, **46**, 1682 (1913).

#### 5.7.2.2.3. with Aryldiazonium Salts.

Arene-diazonium salts,  $\text{ArN}_2\text{X}$ , react with Hg metal in aq acid<sup>1</sup> or in acetone<sup>2</sup> to give  $\text{ArHgX}$ :



Vigorous stirring by specially designed stirrers is essential for good yields. Finely divided Hg, formed<sup>3,4</sup> in situ from  $\text{HgCl}_2$  and  $\text{SnCl}_2$ , is used also:



Functional substituents, including halo, carbonyl or hydroxyl, are tolerated.

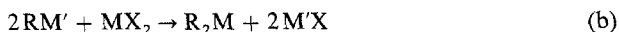
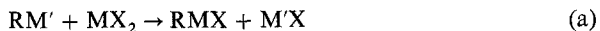
(J. L. WARDELL)

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2. W. Waters, *J. Chem. Soc.*, 2007 (1937).
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#### 5.7.2.3. from Metal Salts

##### 5.7.2.3.1. with Organometallics.

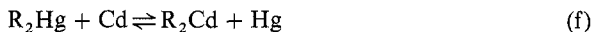
Interactions of Zn, Cd or Hg salts ( $\text{MX}_2$ ) with organic derivatives of other metals ( $\text{RM}'$ ) can lead to mono- or dialkyl compounds<sup>1,2</sup>:



The metal(II) halides (chloride, bromide or iodide), carboxylates, and other salts find use, including Hg(II) fulminate<sup>3</sup>:



with  $\text{Ph}_2\text{Hg}$  provides 3:1  $\text{Ph}_2\text{Cd}$  and  $\text{Ph}_2\text{Hg}$ :

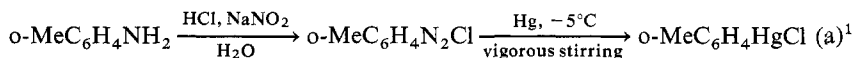


(J. L. WARDELL)

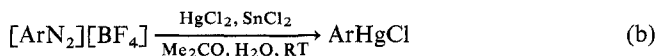
1. R. Taube, D. Steinborn, B. A. Adler, *J. Organomet. Chem.*, **275**, 1 (1984).
2. C. R. McCoy, A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962).
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#### 5.7.2.2.3. with Aryldiazonium Salts.

Arenediazonium salts,  $\text{ArN}_2\text{X}$ , react with Hg metal in aq acid<sup>1</sup> or in acetone<sup>2</sup> to give  $\text{ArHgX}$ :



Vigorous stirring by specially designed stirrers is essential for good yields. Finely divided Hg, formed<sup>3,4</sup> in situ from  $\text{HgCl}_2$  and  $\text{SnCl}_2$ , is used also:



Functional substituents, including halo, carbonyl or hydroxyl, are tolerated.

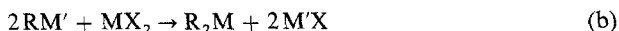
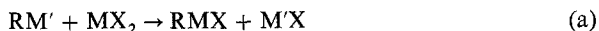
(J. L. WARDELL)

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#### 5.7.2.3. from Metal Salts

##### 5.7.2.3.1. with Organometallics.

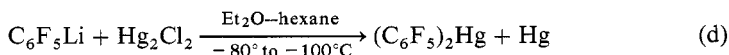
Interactions of Zn, Cd or Hg salts ( $\text{MX}_2$ ) with organic derivatives of other metals ( $\text{RM}'$ ) can lead to mono- or dialkyl compounds<sup>1,2</sup>:



The metal(II) halides (chloride, bromide or iodide), carboxylates, and other salts find use, including  $\text{Hg(II)}$  fulminate<sup>3</sup>:



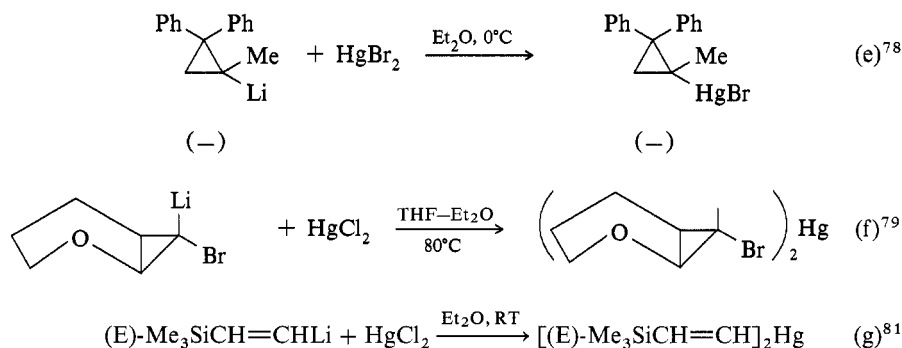
For Hg, Hg(I) halides can be used<sup>4</sup>:



Whether Eq. (a) or Eq. (b) occurs depends on the mole ratio of the reagents: 1 : 1  $\text{RM}' : \text{MX}_2$  forms  $\text{RMX}$ , whereas 2 : 1  $\text{RM}' : \text{MX}_2$  or greater is necessary for  $\text{R}_2\text{M}$ . Other factors include the relative rates of the successive replacements of the anions in  $\text{MX}_2$ .

(i) Transfers from Organolithium and -Magnesium Reagents. The most synthetically useful transmetallating agents are the organomagnesium halides and organolithiums. Organic groups transferred, include primary, secondary or tertiary alkyl, ali- and polycyclic, alkenyl, alkynyl and aryl, as well as some functionally substituted organic groups. The scope of the transmetallations using organomagnesium and -lithium reagents is limited only by the available reagents (see Tables 1 and 2).

As exemplified by organomercury preparations, the transfers of organic groups from Li or Mg can occur with retention of configuration<sup>78-82</sup>:



The solvents are ethers, in particular  $\text{Et}_2\text{O}$  or tetrahydrofuran (THF); higher boiling ethers, such as  $n\text{-Bu}_2\text{O}$ , have more limited use<sup>83</sup>. Hydrocarbon media are used also, e.g., heptane<sup>84</sup> for the formation of  $n\text{-C}_8\text{H}_{17}\text{HgCl}$  in 81 % yield from  $n\text{-C}_8\text{Mg}_{17}\text{MgCl}$ . Aside from those organolithium reagents which are commercially available, organolithium and -magnesium reagents are made in situ. Different solvents can be used to prepare the transmetallating agent and for its subsequent reaction with the group-IIB metal dihalide. To increase T at a later stage of the reaction, a higher boiling solvent can be introduced to the reaction media with the original and lower boiling solvent being distilled. Alternatively, a change of solvent can be used to reduce the polarity or solvating ability of the medium, e.g., in the additions<sup>85</sup> of isooctane to  $n\text{-OctMgBr-ZnCl}_2\text{-Et}_2\text{O}$ , to<sup>86</sup> cycloalkylmagnesium halides- $\text{ZnCl}_2\text{-Et}_2\text{O}$ , or to<sup>87</sup>  $\text{CH}_2=\text{CHCH}_2\text{MgBr-ZnCl}_2\text{-THF}$  and of<sup>88</sup> toluene to  $\text{C}_6\text{F}_5\text{MgBr-ZnCl}_2\text{-Et}_2\text{O}$ .

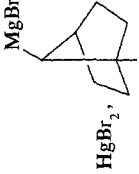
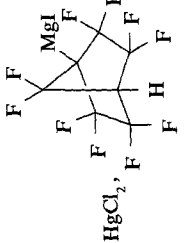
In the formation of  $\text{RMX}$  from group-IIB halides the choice of halide, especially when the transmetallating agent is itself made in situ from an organic halide is important, e.g., use of different halides in these two steps may result in mixed-halide products unless separation is possible.

For organomercury salts, anion exchanges can be used. Although direct addition of  $\text{xs anion, Y}^-$ , to  $\text{RHgX}$  may be sufficient to give  $\text{RHgY}$ , e.g.:



TABLE 1. FORMATION OF ORGANIZINC, -CADMIUM AND -MERCURY COMPOUNDS BY TRANSMETALLATION USING ORGANOMAGNESIUM REAGENTS:

RMgX + MX <sub>2</sub> → RMX or R <sub>2</sub> M		Solvents and conditions	Product	Yield (%)	Ref.
Reagents					
Zinc					
ZnCl <sub>2</sub> -DCH <sub>3</sub> MgBr	Et <sub>2</sub> O		(DCH <sub>3</sub> ) <sub>2</sub> Zn		5
ZnCl <sub>2</sub> -n-BuMgCl	Et <sub>2</sub> O		n-Bu <sub>2</sub> Zn	57	6
ZnCl <sub>2</sub> -n-OctMgBr	Et <sub>2</sub> O		n-Oct <sub>2</sub> Zn	45	85
ZnCl <sub>2</sub> -cyclo-C <sub>3</sub> H <sub>7</sub> MgBr	Et <sub>2</sub> O		(cyclo-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Zn	—	86
ZnCl <sub>2</sub> -cyclo-C <sub>4</sub> H <sub>9</sub> MgBr	Et <sub>2</sub> O		(cyclo-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Zn	19	86
ZnCl <sub>2</sub> -Me <sub>3</sub> SiCH <sub>2</sub> MgCl	Et <sub>2</sub> O, 4 days, RT		(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>2</sub> Zn	90	7
ZnCl <sub>2</sub> -MeO(CH <sub>2</sub> ) <sub>4</sub> MgCl	Et <sub>2</sub> O, RT 1 h		[MeO(CH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub> Zn	20	8
ZnCl <sub>2</sub> -EtS(CH <sub>2</sub> ) <sub>3</sub> MgCl	Et <sub>2</sub> O, RT, 30 min		[EtS(CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> Zn	23	8
ZnCl <sub>2</sub> -PhCH <sub>2</sub> MgBr	(i) Et <sub>2</sub> O (ii) dioxane		(PhCH <sub>2</sub> ) <sub>2</sub> Zn Ph <sub>2</sub> Zn-dioxane	62	9
ZnCl <sub>2</sub> -C <sub>6</sub> F <sub>5</sub> MgBr	Et <sub>2</sub> O		(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Zn	15	84
ZnCl <sub>2</sub> -CH <sub>2</sub> =CHMgBr	THF, 12 h, 55°C		(CH <sub>2</sub> =CH) <sub>2</sub> Zn	—	10
ZnCl <sub>2</sub> -CH <sub>2</sub> =CHCH <sub>2</sub> MgBr	(i) THF, 50°C, 2 h (ii) isooctane; bipy		(CH <sub>2</sub> =CHCH <sub>2</sub> ) <sub>2</sub> Zn	—	87
ZnCl <sub>2</sub> -HC≡CCH <sub>2</sub> MgBr	Et <sub>2</sub> O		(HC≡CCH <sub>2</sub> ) <sub>2</sub> Zn	—	11
Cadmium					
CdCl <sub>2</sub> -MeMgI	Et <sub>2</sub> O		Me <sub>2</sub> Cd	—	12
CdCl <sub>2</sub> -Me <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> MgBr	Et <sub>2</sub> O, RT		[Me <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> Cd	—	13
CdCl <sub>2</sub> -cyclo-C <sub>4</sub> H <sub>9</sub> MgBr	Et <sub>2</sub> O		(cyclo-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Cd	15	14
CdI <sub>2</sub> -Me <sub>3</sub> SiCH <sub>2</sub> MgCl	Et <sub>2</sub> O, 16 h, 25°C		(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>2</sub> Cd	53	106
CdCl <sub>2</sub> -PhCH <sub>2</sub> MgCl	Et <sub>2</sub> O, 1 h, reflux		(PhCH <sub>2</sub> ) <sub>2</sub> Cd	—	15
CdBr <sub>2</sub> -MeCH=CHCH <sub>2</sub> MgBr	Et <sub>2</sub> O, -25°C		(MeCH=CHCH <sub>2</sub> ) <sub>2</sub> Cd	—	16
CdCl <sub>2</sub> -PhMgBr	Et <sub>2</sub> O, RT		Ph <sub>2</sub> Cd	—	17
CdBr <sub>2</sub> -p-ClC <sub>6</sub> H <sub>4</sub> MgBr	(i) Et <sub>2</sub> O, 1 h (ii) dioxane		(p-ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Cd	32	18

$\text{CdBr}_2$ -n-BuMgBr	(i) $\text{Et}_2\text{O}$ (ii) dioxane	n-BuCdBr	19
$\text{CdCl}_2$ - $\text{H}_2\text{C}\equiv\text{CHC}\equiv\text{CCMgBr}$	$\text{Et}_2\text{O}$ -PhH	$\text{H}_2\text{C}\equiv\text{CHC}\equiv\text{CCdBr}$	20
Mercury			
$\text{HgCl}_2$ -MeMgBr	$\text{Et}_2\text{O}$	MeHgBr	21
$\text{HgCl}_2$ -EtHgBr	$\text{Et}_2\text{O}$	EtHgBr	21
$\text{HgCl}_2$ - $\text{C}_{16}\text{H}_{33}\text{MgBr}$	$\text{Et}_2\text{O}$	$\text{C}_{16}\text{H}_{33}\text{HgBr}$	21
$\text{HgCl}_2$ -i-PrMgCl	$\text{Et}_2\text{O}$ , RT, 24 h	i-PrHgCl	22
$\text{HgBr}_2$ -s-BuMgBr	$\text{Et}_2\text{O}$	s-BuHgBr	23
$\text{HgCl}_2$ -t-BuMgCl	$\text{Et}_2\text{O}$	t-BuHgCl	24
$\text{HgBr}_2$ -cis-3-Me-cyclo- $\text{C}_6\text{H}_{10}\text{MgCl}$	$\text{Et}_2\text{O}$	cis-3-Me-cyclo- $\text{C}_6\text{H}_{10}\text{HgBr}$	25
			26
$\text{HgBr}_2$ -PhOCH(OMe)MgBr	THF, 6 h, reflux	PhOCH(OMe)HgBr	27
$\text{HgCl}_2$ - $\text{H}_2\text{C}\equiv\text{CHMgBr}$	THF, 15 h, reflux	$\text{H}_2\text{C}\equiv\text{CHHgCl}$	28
$\text{HgBr}_2$ -BrMg(CH <sub>2</sub> ) <sub>3</sub> MgBr	THF	BrHg(CH <sub>2</sub> ) <sub>3</sub> HgBr	29
$\text{HgCl}_2$ -PhCH <sub>2</sub> MgCl	$\text{Et}_2\text{O}$	PhCH <sub>2</sub> HgCl	30
$\text{HgCl}_2$ -PhMgBr	$\text{Et}_2\text{O}$	PhHgBr	31
$\text{HgCl}_2$ -n-PrMgBr	$\text{Et}_2\text{O}$	n-Pr <sub>2</sub> Hg	32
$\text{HgCl}_2$ -i-PrMgCl	$\text{Et}_2\text{O}$ -THF	i-Pr <sub>2</sub> Hg	32
$\text{HgX}_2$ -cyclo- $\text{C}_3\text{H}_5\text{MgBr}$	THF, 12 h, reflux	(cyclo- $\text{C}_3\text{H}_5$ ) <sub>2</sub> Hg	33
$\text{HgCl}_2$ -Me <sub>2</sub> As(CH <sub>2</sub> ) <sub>3</sub> MgCl		[Me <sub>2</sub> As(CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> Hg	34
			35

(continued)

Table 1. (Continued)

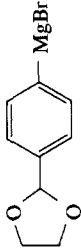
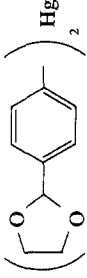
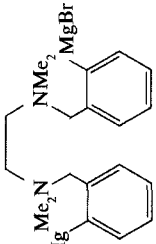
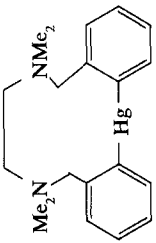
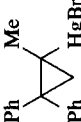
Reagents	Solvents and conditions	Product	Yield (%)	Ref.
$\text{HgCl}_2$ - $\text{CH}_2=\text{CHMgBr}$	THF, 12 h, reflux	$(\text{CH}_2=\text{CH})_2\text{Hg}$	60	33
$\text{HgCl}_2$ - $\text{MeCH}=\text{CHCH}_2\text{MgCl}$	THF, 2 h, 60°C	$(\text{MeCH}=\text{CHCH}_2)_2\text{Hg}$	60	81
$\text{HgCl}_2$ - $\text{o-ClC}_6\text{H}_4\text{CH}_2\text{MgCl}$	$\text{Et}_2\text{O}$ , 3 h, $\Delta$	$(\text{o-ClC}_6\text{H}_4\text{CH}_2)_2\text{Hg}$	36	36
$\text{HgCl}_2$ - $\text{C}_6\text{D}_5\text{MgBr}$	$\text{Et}_2\text{O}$	$(\text{C}_6\text{D}_5)_2\text{Hg}$	34	37
$\text{HgBr}_2$ : 	THF, 3 h, 70°C			38
$\text{HgCl}_2$ - $\text{C}_6\text{F}_5\text{MgBr}$	$\text{Et}_2\text{O}$ , 1 h	$(\text{C}_6\text{F}_5)_2\text{Hg}$	73	39
$\text{HgCl}_2$ - $\text{C}_6\text{Cl}_5\text{MgBr}$	THF, RT	$(\text{C}_6\text{Cl}_5)_2\text{Hg}$	50	40
$\text{HgBr}_2$ :  $\text{BrMg}$	THF $\longrightarrow$		43	41
$\text{HgCl}_2$ - $\text{o-BrMgC}_6\text{H}_4\text{OCH}_2\text{CH}=\text{CH}_2$	THF, reflux	$\text{Hg}(\text{C}_6\text{H}_4\text{OCH}_2\text{CH}=\text{CH}_2\text{o})_2$	73	42
$\text{HgBr}_2$ - $3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{MgBr}$	$\text{Et}_2\text{O}$ , THF, 100°C, 2½ h	$3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{HgBr}$	50	43

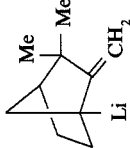
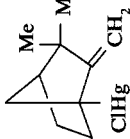
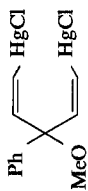
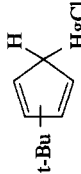

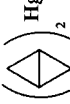
TABLE 2. FORMATION OF ORGANOZINC, -CADMIUM AND -MERCURY COMPOUNDS BY TRANSMETALLATION USING ORGANOLITHIUM AND OTHER ALKALI METAL REAGENTS

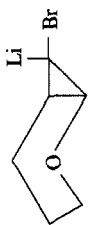
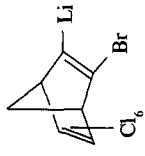
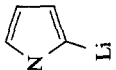
Reagents	Solvent and conditions	Product	Yield (%)	Ref.
<b>Zinc</b>				
$\text{ZnCl}_2\text{-ClCH}_2\text{Li}$	$\text{THF-Et}_2\text{O}$ , $-74^\circ\text{C} \rightarrow \text{RT}$	$(\text{ClCH}_2)_2\text{Zn}$	—	44
$\text{ZnCl}_2\text{-(Me}_3\text{Si)}_3\text{CLi}$	$\text{THF-Et}_2\text{O}$ , 20 h, $20^\circ\text{C}$	$[(\text{Me}_3\text{Si})_3\text{Cl}]_2\text{Zn}$	33	45
$\text{ZnCl}_2\text{-PhLi}$	$\text{Et}_2\text{O}$	$\text{Ph}_2\text{Zn}$	65	46
$\text{ZnCl}_2\text{-o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}$	$\text{Et}_2\text{O}$ , hexane	$(\text{o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Zn}$		47
$\text{ZnCl}_2\text{-C}_3\text{H}_5\text{Na}$		$(\text{C}_3\text{H}_5)_2\text{Zn}$		48
$\text{ZnCl}_2\text{-Ph}_2\text{CHNa-dioxane}$	$\text{Et}_2\text{O-THF}$ , $-78^\circ\text{C}$	$(\text{Ph}_2\text{CH})_2\text{Zn}$		49
$\text{ZnCl}_2\text{-C}_3\text{H}_5\text{K}$	$\text{THF}$ , $-20^\circ\text{C}$	$(\text{CH}_2=\text{CHCH}=\text{CHCH}_2)_2\text{Zn}$	67	50
<b>Cadmium</b>				
$\text{CdCl}_2\text{-(Me}_3\text{Si)}_2\text{CHLi}$	$\text{Et}_2\text{O}$ , $4\frac{1}{2}$ h, $\Delta$	$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Cd}$	34	51
$\text{CdCl}_2\text{-(Me}_3\text{Si)}_3\text{CLi}$	$\text{Et}_2\text{O-THF}$ , 20 h, $20^\circ\text{C}$	$[(\text{Me}_3\text{Si})_3\text{Cl}]_2\text{Cd}$	22	45
$\text{CdBr}_2\text{-PhLi}$	$\text{Et}_2\text{O}$	$\text{Ph}_2\text{Cd}$	43	46
$\text{CdI}_2\text{-o-LiC}_6\text{H}_4\text{C}_6\text{H}_4\text{Li-o}$	$\text{Et}_2\text{O}$ , $70^\circ\text{C}$	$[\text{o-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Cd-o}]_n$		52
$\text{CdCl}_2\text{-C}_6\text{F}_5\text{Li}$	$\text{Et}_2\text{O}$ , $-78^\circ\text{C} \rightarrow \text{RT}$	$(\text{C}_6\text{F}_5)_2\text{Cd}$	51	53
$\text{Cd(SCN)}_2\text{-PhC}\equiv\text{CK}$	$\text{liq NH}_3$	$(\text{PhC}\equiv\text{C})_2\text{Cd}$	25	54
<b>Mercury</b>				
$\text{HgBr}_2$	$\text{Et}_2\text{O}$ , $0^\circ\text{C}$		37	78
$\text{HgBr}_2\text{-[Ph}_2\text{P(O)}]_2\text{CHLi}$				
$\text{HgCl}_2\text{-LiCH}_2\text{CN}$	$\text{THF-benzene}$	$[\text{Ph}_2\text{P(O)}]_2\text{CHHgBr}$	90	65
	$\text{THF}$ , $70^\circ\text{C}$	$\text{CHHgCH}_2\text{CN}$	60	56
$\text{HgCl}_2\text{-cis-MeCH}=\text{CHLi}$		$[\text{+20\% Hg(CH}_2\text{CN)}_2]$		
$\text{HgCl}_2\text{-trans-MeCH}=\text{CHLi}$		$\text{cis-MeCH}=\text{CHHgBr}$	77	80
$\text{HgCl}_2\text{-CCl}_2\text{CH}=\text{CH}_2\text{Li}$		$\text{trans-MeCH}=\text{CHHgBr}$	80	80
	$\text{THF}$ , $-105^\circ\text{C}$	$\text{CCl}_2=\text{CHCH}_2\text{HgCl}$	21	57

(continued)

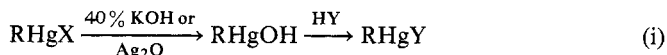


Table 2. (Continued)

Reagents	Solvent and conditions	Product	Yield (%)	Ref.
$\text{HgCl}_2$ 			59	
$\text{HgCl}_2-(\text{LiCH}=\text{CH})_2\text{CPh(OMe)}$	$\text{Et}_2\text{O}$		60	
$\text{HgCl}_2-t\text{-BuC}_3\text{H}_7\text{Li}$ $\text{HgBr}_2-o\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{Li}$ $\text{HgCl}_2-h^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_3(\text{CH}_2\text{NMe}_2)\text{Li-o}$ $\text{HgBr}_2-(\text{CO})_3\text{ReC}_5\text{H}_4\text{Li}$	THF THF, RT $\text{Et}_2\text{O}$	 $+ (t\text{-BuC}_3\text{H}_7)_2\text{Hg}$ $o\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{HgBr}$ $h^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_3(\text{CH}_2\text{NMe}_2)\text{HgCl-o}$ $(\text{CO})_3\text{ReC}_5\text{H}_4\text{HgBr}$	40 72 63	61 62 63
$\text{HgCl}_2$ ;  Li·TMED	THF		75	64

$\text{HgCl}_2\text{-PhSCH}_2\text{Li}$	THF	$(\text{PhSCH}_2)_2\text{Hg}$	ca. 100	65
$\text{HgBr}_2\text{-PhSO}_2\text{CH}_2\text{Li}$	$\text{Et}_2\text{O-THF}$	$(\text{PhSO}_2\text{CH}_2)_2\text{Hg}$	78	66
$\text{HgBr}_2\text{-(PhS)}_2\text{CHLi}$	THF, $0^\circ\text{C}$	$[(\text{PhS})_2\text{CH}]_2\text{Hg}$	75	67
$\text{HgCl}_2\text{-(Me}_3\text{Si)}_2\text{CHLi}$	$\text{Et}_2\text{O}$	$[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Hg}$		51
$\text{HgCl}_2\text{-Li}$ 	THF- $\text{Et}_2\text{O}$ , $80^\circ\text{C}$	$(\text{bicyclic})_2\text{Hg}$	10	68
$\text{HgCl}_2\text{-Li}$ 		$(\text{bicyclic})_2\text{Hg}$		69
$\text{HgCl}_2\text{-CH}_2=\text{CClLi}$	THF-petroleum ether, $-10^\circ\text{C}$	$(\text{CH}_2=\text{CCl})_2\text{Hg}$	63	70
$\text{HgCl}_2\text{-CF}_2=\text{CFLi}$	$\text{Et}_2\text{O}$ , $0^\circ\text{C}$	$(\text{F}_2\text{C}=\text{CF})_2\text{Hg}$	52	71
$\text{HgCl}_2\text{-MeC}_5\text{H}_3\text{Li}$	THF, $-70^\circ\text{C}$	$(\text{MeC}_5\text{H}_3)_2\text{Hg}$		60
$\text{HgCl}_2\text{-o-LiC}_6\text{H}_4\text{N}$ 	(i) $\text{Et}_2\text{O}$ (ii) $\text{H}_2\text{O}$	$(\text{bicyclic})_2\text{Hg}$	38	72
$\text{HgCl}_2\text{-o-LiC}_6\text{H}_4\text{Li-o}$	$\text{Et}_2\text{O}$	$[\text{o-C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg-o}]_3$		73
$\text{HgCl}_2\text{-o-BrC}_6\text{F}_4\text{Li}$	$\text{Et}_2\text{O}$ , $-70^\circ\text{C}$	$(\text{o-BrC}_6\text{F}_4)_2\text{Hg}$	94	74
$\text{HgCl}_2\text{-h}^5\text{-C}_5\text{H}_3\text{FeC}_3\text{H}_3(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Li-o}$	$\text{Et}_2\text{O}$	$[\text{h}^5\text{-C}_5\text{H}_3\text{FeC}_3\text{H}_3(\text{CH}_2\text{CH}_2\text{NMe}_2)]_2\text{Hg}$	12	75
$\text{HgCl}_2\text{-C}_5\text{H}_5\text{Na}$	THF, $-30^\circ\text{C}$	$(\text{C}_5\text{H}_5)_2\text{Hg}$	20	76
$\text{HgCl}_2\text{-o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}$	$\text{Et}_2\text{O}$ , THF, RT	$(\text{o-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Hg}$		77

intermediate stages are favored, e.g.:

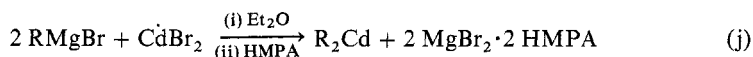


Such steps are incorporated as purification steps into syntheses of organomercury salts.

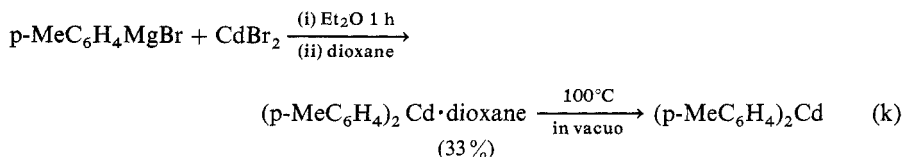
When the transmetallating agent is made in situ from the metal, filtration is performed to remove unused metal before the metal halide is added.

The group-IIB metal dihalide is added to the solution of the transmetallating reagent either in small portions or in solution. The solubility of Hg(II) halides is not considerable, even in ether, and if solid  $\text{HgX}_2$  is added, vigorous stirring is advisable.

A donor such as hexamethylphosphoramide (HMPA)<sup>90</sup>, dioxane<sup>83,91</sup> or bipy<sup>87</sup>, also can be added toward the end of the transmetallation to enable easier separation of the organometallic product from the metal halides present. This is particularly useful for organozinc and -cadmium preparations, because the reaction media cannot be treated with  $\text{H}_2\text{O}$  to separate the metal halides, e.g., addition of HMPA<sup>90</sup> to an  $\text{Et}_2\text{O}$  solution containing an organocadmium product and Mg salts,  $\text{MgX}_2$ , results in precipitation of  $\text{MgX}_2 \cdot 2 \text{HMPA}$ , thereby leaving  $\text{R}_2\text{Cd}$  in solution free of Mg halides, e.g.:



Similar procedures involving dioxane are employed for  $\text{ZnCl}_2\text{-RMgX}$ <sup>83,91</sup>. These treatments with donor molecules (D) result in formation of complexes,  $\text{RMX} \cdot \text{D}$  and  $\text{R}_2\text{M} \cdot \text{D}$  (e.g.,  $\text{M} = \text{Cd}$  or  $\text{Zn}$ ). The organometallic compound can be freed on heating in vacuo, e.g.<sup>91</sup>:



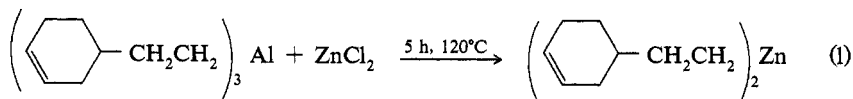
Organozincs and -cadmiums are reactive towards  $\text{O}_2$ , e.g., the **alkylzincs inflame in air**. Hence, **care must be taken to exclude air and to provide an inert atmosphere**, such as  $\text{CO}_2$  or  $\text{N}_2$ , during the preparations. The reactivity of organozincs and -cadmiums toward proton sources makes it essential also to avoid contact with  $\text{H}_2\text{O}$ .

Hydrolyses and oxidations are not problems with organomercurials; xs transmetalating agents,  $\text{RLi}$  or  $\text{RMgX}$ , may be removed by hydrolysis. The differences in properties of  $\text{RHgX}$  (high mp, polar—if not ionic) and  $\text{R}_2\text{Hg}$  (more volatile and nonpolar, with appreciable solubility in nonpolar solvents) must be considered in designing workup procedures.

**Care must be exercised in handling toxic organomercurials.**

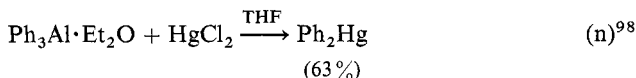
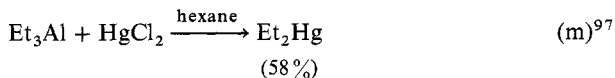
Organic derivatives of other metals may also act as transmetallating agents.

(ii) Transfer from Organoaluminum Compounds. Organoaluminums are used to prepare organozinc, -cadmium and -mercury compounds; e.g., trimethylaluminum reacts with<sup>92</sup>  $\text{Zn}(\text{OAc})_2$  or<sup>93</sup>  $\text{ZnI}_2$  to give  $\text{Me}_2\text{Zn}$ . Diethylzinc can be prepared from  $[\text{Et}_4\text{Al}]\text{Na}$  (92% yield)<sup>94</sup> or  $\text{Et}_2\text{AlCl}$  (10%)<sup>95</sup> with zinc halides. Another example is<sup>93</sup>:



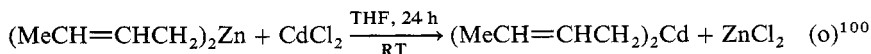
Diethylcadmium is prepared from reaction of  $\text{Et}_3\text{Al}$  with<sup>96</sup>  $\text{Cd}(\text{OAc})_2$  and of  $\text{Et}_2\text{AlCl}$  with  $\text{CdCl}_2$ .

For organomercurials,  $\text{R}_3\text{Al}$  (e.g.,  $\text{R} = \text{Et}$ <sup>97</sup> or  $\text{Ph}$ <sup>98</sup>),  $\text{R}_2\text{AlCl}$ ,  $\text{RAlCl}_2$  (e.g.,  $\text{R} = \text{Me}$  or  $\text{Et}$ <sup>99</sup>) or<sup>99</sup>  $[\text{EtAlCl}_3]\text{Na}$  are all used with  $\text{HgCl}_2$ :

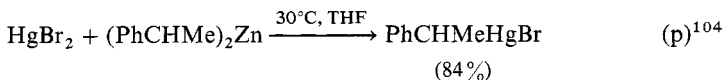


As well as  $\text{HgCl}_2$ ,  $\text{Hg}(\text{OAc})_2$  reacts with  $\text{R}_3\text{Al}$  to give  $\text{R}_2\text{Hg}$ ;  $\text{Hg}(\text{OAc})_2$  is the superior reagent.

(iii) Transfer from Organozincs and -cadmiums. Organozincs are used to prepare organocadmiums:

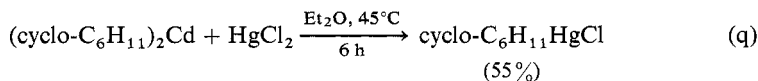


and organomercurials. Various organic groups can be transferred from zinc in good yields. These include  $\text{ICH}_2$ <sup>101</sup>,  $\text{ClCH}_2$ <sup>102</sup>, benzyl<sup>103,104</sup>:

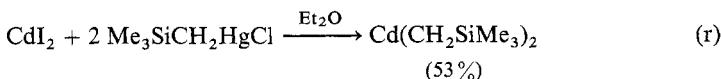


and allyl<sup>103</sup> and  $\text{PhC}\equiv\text{CCH}_2$ <sup>103</sup>, the reactions taking place in THF.

Organic groups also can be transferred<sup>105</sup> from  $\text{Cd}$  to  $\text{Hg}$ , e.g.:



Reaction in the reverse sense, i.e., organic group transfer from  $\text{Hg}$  to  $\text{Cd}$ , also occurs<sup>106</sup>:



(iv) Transfers from Organoboranes. Use is made of organoborane- $\text{Hg}$  salt reactions<sup>107-113</sup> to prepare organomercurials (Table 3). Related reactions with organoboronic acids and esters are discussed in §5.7.2.3.7.i. These transmetalations are valuable for alkyl- and alkenylboranes, which can be prepared by hydroboration of alkenes and alkynes but not for other organoboranes such as arylboranes. The latter are prepared from organomagnesium halides or organolithiums, which can be used directly with  $\text{Hg}$  salts.

Primary alkyl groups can be transferred from triorganoboranes to  $\text{Hg}$  using carboxylates at RT in THF, and all three primary alkyl groups can react to give either organomercury salts, e.g.<sup>107-109</sup>:

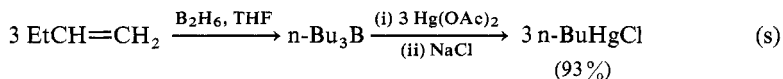
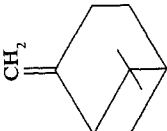
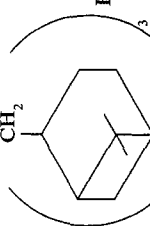
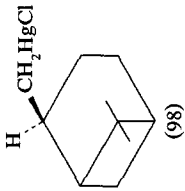


TABLE 3. PREPARATION OF ORGANOMERCURIALS FROM ORGANOBORANES

Starting material	Hydroboration reagent <sup>a</sup>	Organoborane	Conditions for alkyl transfer	Product (yield, %)	Ref.
$\text{EtCH}=\text{CH}_2$	A	$n\text{-Bu}_3\text{B}$	(i) $\text{Hg}(\text{OAc})_2$ (3 equiv), THF (ii) $\text{NaCl}$ , $\text{H}_2\text{O}$	$n\text{-BuHgCl}$ (93)	108
$n\text{-C}_{10}\text{H}_{21}\text{CH}=\text{CH}_2$	A	$(n\text{-C}_{12}\text{H}_{25})_3\text{B}$	(i) $\text{Hg}(\text{OAc})_2$ (3 equiv), THF (ii) $\text{NaCl}$ , $\text{H}_2\text{O}$	$n\text{-C}_{12}\text{H}_{25}\text{HgCl}$ (98)	108
$n\text{-BuCH}=\text{CH}_2$	B	$n\text{-C}_6\text{H}_{13}\text{BR}_2^b$	(i) $\text{Hg}(\text{OAc})_2$ (1 equiv), THF (ii) $\text{NaCl}$ , $\text{H}_2\text{O}$	$n\text{-C}_6\text{H}_{13}\text{HgCl}$ (98)	108
$\text{PhCH}=\text{CH}_2$	B	$\text{PhCH}_2\text{CH}_2\text{BR}_2^b$	(i) $\text{Hg}(\text{OAc})_2$ (1 equiv), THF (ii) $\text{NaCl}$ , $\text{H}_2\text{O}$	$\text{PhCH}_2\text{CH}_2\text{HgCl}$ (99)	108
$\text{PhMeC}=\text{CH}_2$	A	$(\text{PhMeHCH}_2)_3\text{B}$	(i) $\text{Hg}(\text{OAc})_2$ (3 equiv), THF (ii) $\text{NaCl}$ , $\text{H}_2\text{O}$	$\text{PhMeCH}=\text{CH}_2\text{HgCl}$ (97)	108
	A		(i) $\text{Hg}(\text{OAc})_2$ (3 equiv), THF (ii) $\text{NaCl}$ , $\text{H}_2\text{O}$		108

cyclohexane	A	(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> B	(i) Hg <sub>2</sub> (OMe) <sub>2</sub> , THF (ii) NaCl, H <sub>2</sub> O	cyclo-C <sub>6</sub> H <sub>11</sub> HgCl (60-70) <sup>c</sup>	114
	A	(cyclo-C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> B	(i) Hg <sub>2</sub> (OBU-t) <sub>2</sub> , t-BuOH (ii) NaCl, H <sub>2</sub> O	cyclo-C <sub>6</sub> H <sub>11</sub> HgCl (83) <sup>c</sup>	114
Norbornene	A	(exo-norbornyl) <sub>3</sub> B	(i) Hg <sub>2</sub> OBU-t <sub>2</sub> , t-BuOH (ii) NaCl, H <sub>2</sub> O	exo-norbornylHgCl (82) <sup>c</sup>	114
EtCH=CH <sub>2</sub>	A	n-Bu <sub>3</sub> B	Hg(OAc) <sub>2</sub> (1.5 equiv), THF	n-Bu <sub>2</sub> Hg (71)	110
n-C <sub>10</sub> H <sub>21</sub> CH=CH <sub>2</sub>	A	(n-C <sub>10</sub> H <sub>21</sub> ) <sub>3</sub> B	Hg(OAc) <sub>2</sub> (1.5 equiv), THF	(n-C <sub>10</sub> H <sub>21</sub> ) <sub>2</sub> Hg (83)	110
PhCH=CH <sub>2</sub>	A	(PhCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> B	Hg(OAc) <sub>2</sub> (1.5 equiv), THF	(PhCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> Hg (83)	110
2-CH <sub>2</sub> =CHC <sub>10</sub> H <sub>7</sub> <sup>d</sup>	B	2-C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>2</sub> BR <sub>2</sub> <sup>b</sup>	Hg(OAc) <sub>2</sub> (1.5 equiv), THF	(2-C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> Hg (71)	110
n-PrC≡CH	B	(E)n-PrCH=CHBR <sub>2</sub> <sup>b</sup>	Hg(OAc) <sub>2</sub> , THF, 0°C	(E)n-PrCH=CHHgOAc (85)	115
t-BuC≡CH	B	(E)t-BuCH=CHBR <sub>2</sub> <sup>b</sup>	Hg(OAc) <sub>2</sub> , THF, 0°C	(E)t-BuCH=CHHgOAc (96)	115
EtC≡CEt	B	(Z)-EtCH=CEtBR <sub>2</sub> <sup>b</sup>	Hg(OAc) <sub>2</sub> , THF, 0°C	(E)-EtCH=CEtHgOAc (59)	115
Me <sub>2</sub> △=CH <sub>2</sub> Me <sub>2</sub>	C	Me <sub>2</sub> △HCH <sub>2</sub> HgR <sup>e</sup> Me	Hg(OAc) <sub>2</sub> , THF, pentane	(Me△HCH <sub>2</sub> ) <sub>2</sub> Hg Me <sub>2</sub>	116

<sup>a</sup> A = BH<sub>3</sub>; B = (cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>BH; C = 9-borabicyclo[3.3.1]nonane(9-BBN).

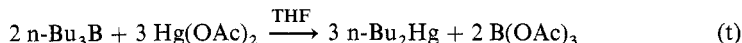
<sup>b</sup> R = cyclo-C<sub>6</sub>H<sub>11</sub>.

<sup>c</sup> Yields based on two organic groups.

<sup>d</sup> C<sub>10</sub>H<sub>7</sub> = naphthyl.

<sup>e</sup> R' = 9-borabicyclo[3.3.1]nonyl.

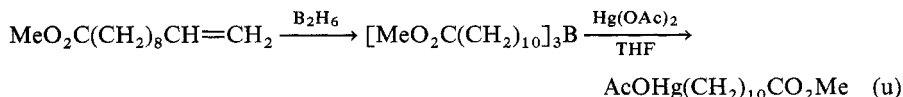
or diorganomercurials, e.g.<sup>110</sup>:



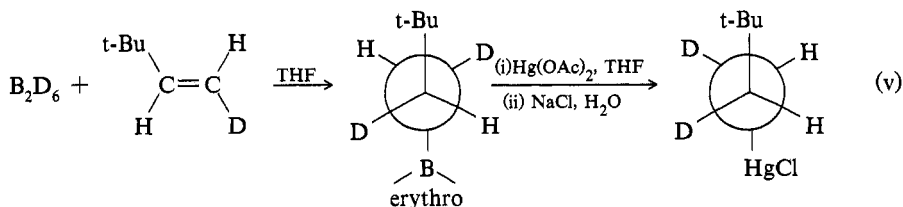
depending on the ratio of reagents and conditions.

Mercurideboronation in alkaline media also produces diorganomercurials<sup>111</sup>. The first two groups react quickly, with the third less reactive.

Ester groups<sup>108</sup> survive the hydroboration-mercurideboronation sequence (i.e., from alkene or organomercurials, e.g.):

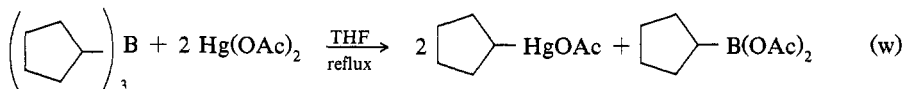


The transfer of alkyl groups occurs with inversion of configuration, e.g.<sup>112</sup>:



The reactivity sequence for  $\text{HgX}_2$  toward primary alkylboranes in THF is  $\text{X} = \text{NO}_3 > > \text{CF}_3\text{CO}_2 \approx \text{F} \approx \text{OAc}$ , with  $\text{HgCl}_2$  and  $\text{HgBr}_2$  being unreactive<sup>109</sup>.

Transfer of secondary alkyl groups from boron to Hg does not occur under the mild conditions used for primary groups<sup>113</sup>; e.g., in THF,  $\text{n-Bu}_3\text{B}$  completely reacts in  $< 5$  min at  $0^\circ\text{C}$ ,  $\text{i-Bu}_3\text{B}$  requires 20–30 min at  $0^\circ\text{C}$ , whereas with  $\text{s-Bu}_3\text{B}$  less than 5% reaction occurs on refluxing for 15 h<sup>113</sup>. However, refluxing in THF can lead to transfer of s-alkyl groups, although only two such groups can be transferred, e.g.:

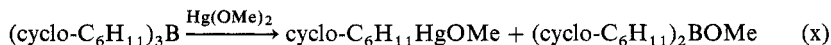


More drastic conditions can lead to secondary decompositions.

The reactivity of tris(s-alkyl)boranes toward  $\text{Hg(O}_2\text{CPh)}_2$  is cyclopentyl  $>$  cyclohexyl  $>$  cyclooctyl  $>$  s-Bu  $>$  norbornyl<sup>113</sup>. The reactivity of  $\text{HgX}_2$  toward secondary alkylboranes is  $\text{X} = \text{NO}_3 > \text{CF}_3\text{CO}_2 > \text{PhCO}_2 > \text{F} > \text{OAc} > \text{phthalate}$ <sup>113</sup>.

Retention of configuration is found for tris-(exo-norbornyl)borane reactions<sup>113</sup>.

Transfer of s-alkyl groups occurs more readily when  $\text{Hg(I)}$  and  $\text{Hg(II)}$  alkoxides are used<sup>114</sup>, the former being the superior reagents. For  $\text{Hg(OMe)}_2$  only one cyclohexyl or other secondary group is transferred, e.g.:

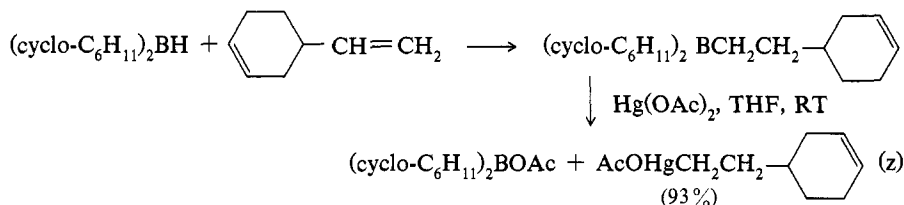


whereas with  $\text{Hg}_2(\text{OMe})_2$  or  $\text{Hg}_2(\text{OBu-t})_2$  two react, e.g.:

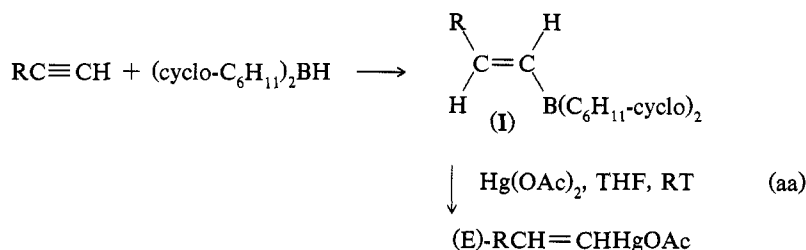


The alkoxides induce radical reactions having induction periods. Some loss of configuration is found with norbornylboranes; e.g., from 99% pure tris(exo-norbornyl)borane, only 80–85% exo-norbornylmercury alkoxides are obtained.

That s-alkyl groups do not react under such mild conditions as primary alkyl groups do enables dicyclohexylborane and borabicyclo[3.3.1]nonane to be used in hydroboration-mercurideboronation sequences, e.g.:

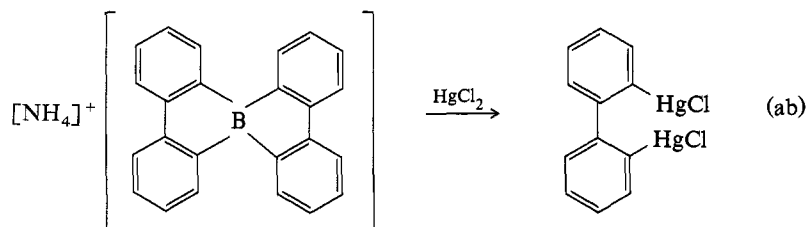


Alkenyl groups can also be transferred from boranes to Hg with retention of configuration, e.g.<sup>115</sup>:

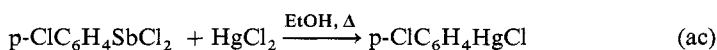


Alkenyl groups are transferred in preference to s-alkyl groups. The yields of trans-alkenylmercurials from  $\text{RC}\equiv\text{CH}$  are greater than 85%; yields from internal alkynes are lower. Use of (I) rather than tris(alkenyl)boranes leads to higher yields of alkenylmercurials.

Transfers of organic groups from  $\text{M}[\text{BR}_4]$  are known, e.g.<sup>117</sup>:



(v) Transfers from Organoantimony or -Bismuth. Organic groups are transferred from Sb and Bi to  $\text{Hg}$ <sup>118</sup>:

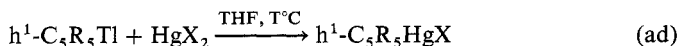


Organobismuth compounds are more reactive toward  $\text{HgCl}_2$  than are the corresponding organoantimony species<sup>119</sup>. Solvent influences are important for triarylantimony- $\text{HgCl}_2$  reactions<sup>120</sup>; e.g., in THF aryl transfer occurs to give  $\text{ArHgCl}$  and  $\text{Ar}_2\text{SbCl}$ ,



whereas in benzene a redox reaction results, with formation of  $\text{Hg}_2\text{Cl}_2$  and  $\text{Ar}_3\text{SbCl}_2$ .

(vi) Transfers from Organothallium Compounds. Both cyclopentadienyl<sup>121</sup> and pentachlorocyclopentadienyl<sup>122</sup> groups transfer from Tl to Hg:



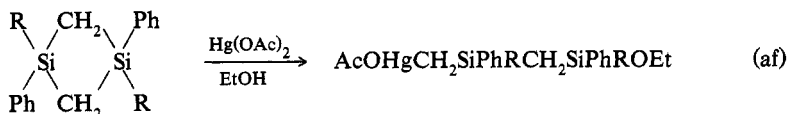
where if  $\text{R} = \text{H}$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$  and  $\text{T} = -40^\circ\text{C}$ ; if  $\text{R} = \text{Cl}$ ,  $\text{X} = \text{Cl}$  and  $\text{T} = -78^\circ\text{C}$ .

(vii) Transfers from Organo-Group-IVB Metal Compounds. Cleavage of organosilicon and other organo-group-IVB metal bonds can occur on reaction with Hg salts to give organomercurials.

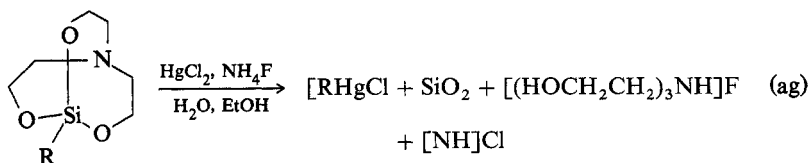
Silacyclobutane derivatives open<sup>123,124</sup>, e.g.:



where<sup>123</sup>  $\text{R}'$ ,  $\text{R}'' = \text{Me}$ ,  $\text{Ph}$ ;

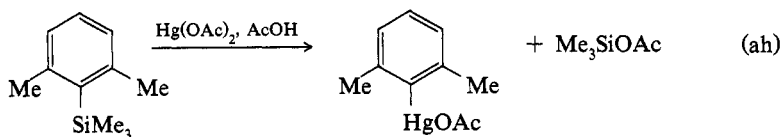


where<sup>124</sup>  $\text{R}$  (yield, %) =  $\text{Me}$  (72),  $\text{Ph}$  (91). Acyclic alkylsilicon bonds also are cleaved by Hg salts<sup>125</sup>, e.g.:



where  $\text{R}$  (yield, %) =  $\text{Me}$  (57),  $\text{CH}_2 = \text{CH}$  (89),  $\text{Ph}$  (60).

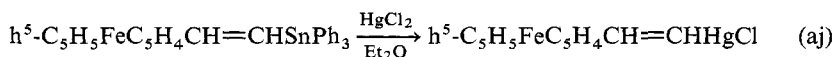
Arylsilicon bonds are more readily cleaved by Hg salts, especially with arylsilane- $\text{Hg}(\text{OAc})_2$ , e.g.<sup>126-129</sup>:



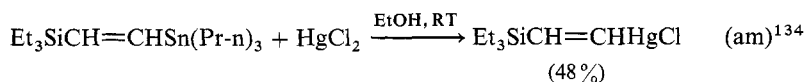
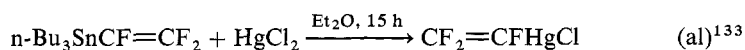
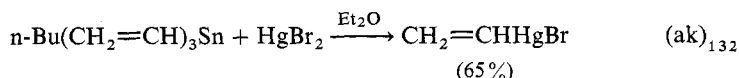
Organotin-Hg salt reactions follow the same trends with phenyltin bonds being more easily cleaved than simple alkyl or even some functionally substituted<sup>130</sup> alkyltin bonds, e.g.:



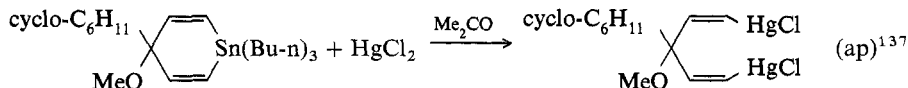
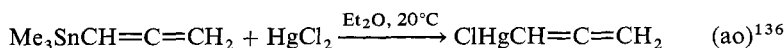
where  $n = 1 - 4$ . However, the ferrocenylvinyltin bond reacts with  $\text{HgCl}_2$  in preference to phenyltin bonds<sup>131</sup>:



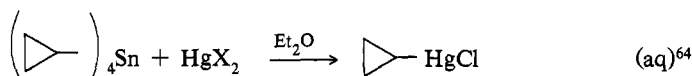
Vinyl<sup>132-134</sup>, allylic<sup>135</sup>, allenic<sup>136</sup> and other alkenyl groups<sup>137</sup> are cleaved from Sn by  $\text{HgX}_2$  and such reactions are useful syntheses of organomercurials, e.g.:



where  $\text{M} = \text{Ge}$  or  $\text{Sn}$ ;

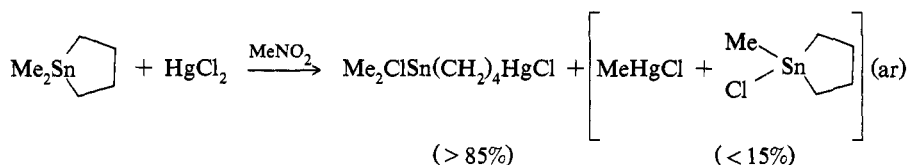


In addition, transfer of cyclopropyl from tetracyclopropyltin to Hg leads<sup>138</sup> to cyclopropylmercury(II) chloride:



where  $\text{X} = \text{Cl}$  or  $\text{Br}$ .

As seen in Eq. (am), a  $\text{Sn}-\text{C}$  bond is more reactive than a  $\text{Si}-\text{C}$  bond. Metal-allyl bonds, as shown in Eq. (an), are cleaved without rearrangement. Retention of configuration results with vinyl group transfers. Ring openings of stannacycloalkanes also can occur, e.g.<sup>139</sup>:



In contrast, reaction with 1,1-dimethylstannacyclohexane occurs to at least 95% at the methyltin bond to give<sup>139</sup> 1-chloro-1-methylstannacyclohexane and  $\text{MeHgCl}$ .

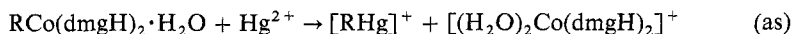
Organolead bonds are the most reactive of the organo-group-IVB bonds, but reactions with  $\text{HgX}_2$  have little synthetic value<sup>140</sup>.

Many  $\text{HgX}_2$ -organo-group-IVB metal reactions have little synthetic value and are studied only for kinetic and mechanistic reasons. The reactions are electrophilic aromatic substitutions for arylmetal cleavages<sup>141</sup> and  $\text{S}_{\text{E}}2$  reactions for alkyltin cleavages<sup>142,143</sup>. Electron-donating substituents lead to increased reactivities for aryl-metal bonds; for tetraalkyltins the reactivity sequence in 96% MeOH toward  $\text{HgCl}_2$  is<sup>143</sup>  $\text{Me}_4\text{Sn} > \text{Et}_4\text{Sn} > n\text{-Pr}_4\text{Sn} > n\text{-Bu}_4\text{Sn} > i\text{-Pr}_4\text{Sn}$ . The transition states for the  $\text{S}_{\text{E}}2$  reactions may be open or cyclic; the former being the accepted view<sup>144-146</sup>.

Mercury(I) salts also are used<sup>147</sup>, e.g.,  $\text{Hg}_2(\text{OAc})_2$  with  $\text{Me}_4\text{Sn}$  or  $(\text{CH}_2=\text{CH})_4\text{Sn}$ , and  $\text{Hg}_2(\text{NO}_3)_2$  with tetraalkyllead compounds.

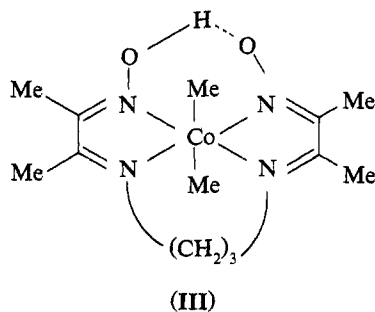
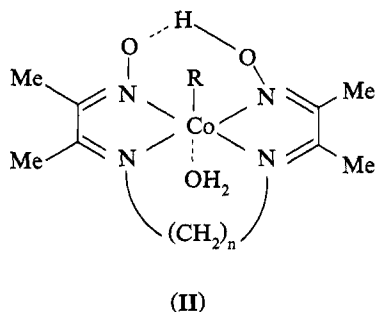
(viii) Transfers from Transition-Metal Compounds.  $\sigma$ -Bonded organo-transition-metal compounds react with  $\text{HgX}_2$  to give organomercurials (see Table 4). Such reactions have synthetic use, e.g., the formation of fluorenylmercury chloride,  $\text{FlHgCl}$ , from  $\text{Fl}_2\text{ZrCl}_2$  and  $\text{HgCl}_2$  in  $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$  (Fl = fluorenyl). Attempts to make this compound (or  $\text{Fl}_2\text{Hg}$ ) from  $\text{FINa}$  or  $\text{Fili}$  fail<sup>147</sup>.

Transfers from organocobalt<sup>166-174</sup> include the generation<sup>167</sup> of  $\text{MeHg(II)}$  by the action of methylcobalamin on  $\text{Hg}^{2+}$ , e.g.:



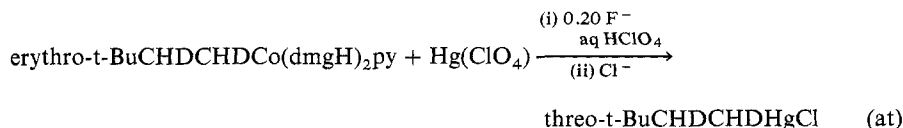
where  $\text{dmgH}$  = dimethylglyoxime.

Chelated cobalt complexes related to methylcobalamin are well studied, e.g., (II):



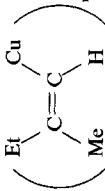
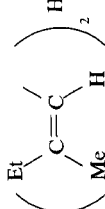
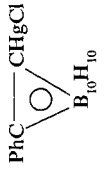
The rate of dealkylation of (II) by  $\text{Hg}^{2+}$  to give  $[\text{RHg}]^+$  is<sup>175</sup>  $\text{R} = \text{Me} \gg \text{Et} > \text{PhCH}_2 > n\text{-Bu} \approx i\text{-Pr}$ . The mechanisms of these reactions are  $\text{S}_{\text{E}}2$ . Methyl transfer to  $\text{Zn}^{2+}$  or  $\text{Cd}^{2+}$  is also possible from (III)<sup>176</sup>.

The stereochemistry of the transfers from organo-transition-metal compounds to  $\text{Hg}^{2+}$  include retention when alkyl groups are cleaved from threo- $\text{RCHDCHDFe}(\text{CO})_2\text{C}_5\text{H}_5\text{-h}^5$  ( $\text{R} = t\text{-Bu}$  or  $\text{Ph}$ )<sup>177</sup> and from<sup>178</sup> trans-threo- $\text{PhCHDCHDW}(\text{CO})_2(\text{PEt}_3)\text{C}_5\text{H}_5\text{-h}^5$ ; but inversion from<sup>177</sup> cis-threo- $\text{PhCHDCHDMn}(\text{CO})_4\text{PEt}_3$  and from<sup>179</sup> erythro- $t\text{-BuCHDCHDCo(dmgH)}_2\text{py}$ <sup>174</sup>:



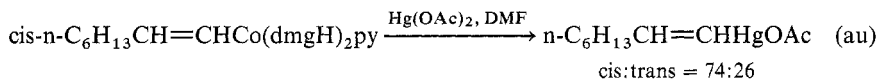
where py is pyridine.

TABLE 4. FORMATIONS OF ORGANOMERCURIALS FROM MERCURY(II) SALTS WITH  
 $\sigma$ -BONDED TRANSITION-METAL COMPOUNDS

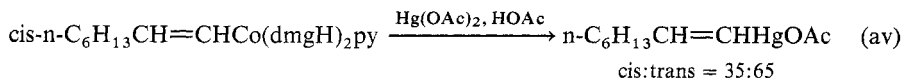
Transition-metal compounds	Mercury salt and conditions	Product (yield, %)	Ref.
$(RC \equiv CCu)_n$ (R = alkyl, vinyl or aryl)	HgCl <sub>2</sub> , THF	$(RC \equiv C)_2Hg$	148
	HgBr <sub>2</sub> , THF, -40°C		149
$(\sigma-Cu_6C_6H_4CH_3PPh_3)_n$	HgBr <sub>2</sub> , THF, 20°C	$\sigma-BrHgC_6H_4CH_3PPh_3 \cdot CuBr$ (81)	150
$(CO)_3Mn(h^5-C_5H_4Cu)_n$	HgCl <sub>2</sub> , PhH	$(CO)_3Mn(h^5-C_5H_4HgCl)$ (94)	151
$[(CF_3)_2CHAg]_n$	HgCl <sub>2</sub> , MeCN	$[(CF_3)_2CH]_2Hg$ (49)	152
$(C_6F_5Ag)_n$	HgBr <sub>2</sub> , Et <sub>2</sub> O, 25°C	$(C_6F_5)_2Hg$	153
$(C_6F_5Ag)_n$	ZnI <sub>2</sub> , Et <sub>2</sub> O	$(C_6F_5)_2Zn$	153
$(h^5-C_5H_4Cl)Fe(C_5H_4Ag-h^5)$	HgCl <sub>2</sub> , PhH, RT	$(h^5-C_5H_4Cl)Fe(h^5-C_5H_4HgCl)$ (96)	154
$(CO)_3Mn-C_5H_4Ag-h^5$	HgCl <sub>2</sub> , PhH	$(CO)_3Mn(h^5-C_5H_4HgCl)$ (86)	155
$[p-MeC_6H_4C \equiv NC(OEt)Ag]_3$	HgCl <sub>2</sub> , 2 Ph <sub>3</sub> P	$[p-MeC_6H_4N \equiv C(OEt)]_2Hg$	156
$(PhC \equiv CAg)_n$	HgX <sub>2</sub> , THF, X = Cl, Br or I	$(PhC \equiv C)_2Hg$	157
$RAuPPh_3$ R = Me, Et or BuC(CN)CO <sub>2</sub> Et	HgX <sub>2</sub> -DMF or dioxane, X = Cl, Br, I or OAc	RHgX	158
$PhAu \cdot PPh_3$	HgCl <sub>2</sub>	PhHgCl (82)	159
trans-PhCH=CHAuPPh <sub>3</sub>	HgBr <sub>2</sub> , PhH	trans-PhCH=CHHgBr (97)	160
$h^5-C_5H_5Fe(CO)CH_2CH_2Ph$	HgCl <sub>2</sub>	PhCH <sub>2</sub> CH <sub>2</sub> HgCl (85)	161
$h^5-C_5H_5Fe(CO)CH_2CO-h^5-C_5H_5FeC_3H_5-h^5$	HgBr <sub>2</sub> , Me <sub>2</sub> CO	$h^5-C_5H_5FeC_3H_5COCH_2HgBr-h^5(59)$	162
$h^5-C_5H_5Fe(CO)_2C \equiv CPh$	HgCl <sub>2</sub> , PhMe, 110°C		163
$Fl_2ZrCl_2^a$ $(C_6F_5)_4Zr$	HgCl <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> HgCl <sub>2</sub>	FlHgCl <sup>a</sup> (25) $(C_6F_5)_2Hg$ (89)	164 165

<sup>a</sup> Fl = fluorenyl.

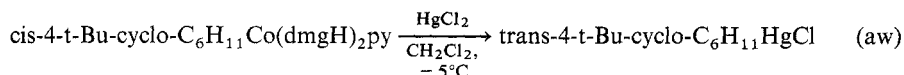
Reaction of  $n\text{-C}_6\text{H}_{13}\text{CH}=\text{CHCo}(\text{dmgH})_2\cdot\text{py}$  with  $\text{Hg}(\text{OAc})_2$  proceeds with predominant retention in  $N,N$ -dimethylformamide (DMF):



but with predominant inversion in <sup>180</sup> acetic acid (HOAc):



Styrylcobaloximes also react with  $\text{Hg}(\text{OAc})_2$  in DMF with retention<sup>181</sup>. Exclusive or preferential inversions occur for cyclohexylcobaloximes<sup>182</sup>:



The mechanism of these reactions leading to retention is  $\text{S}_{\text{E}}(\text{oxidative})$ , whereas an  $\text{S}_{\text{E}}(2)$  open mechanism operates in the reaction leading to inversion. The differences are rationalized by the energy gap between the highest occupied molecular orbital (HOMO) and the metal-carbon  $\sigma$ -bonding orbital for each compound<sup>178</sup>.

(J. L. WARDELL)

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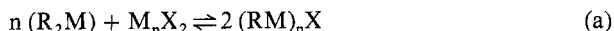
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#### 5.7.2.3.2. by Redistribution with the Organometallics of the Same Metal.

Reactions of diorganometal compounds with salts of the metals, e.g.:

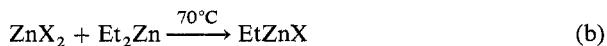


are used to prepare monoorganometallic derivatives<sup>1,2</sup> of Zn, Cd or Hg. In addition to salts of monobasic acids, HX, salts of di- and tribasic acids (H<sub>2</sub>X and H<sub>3</sub>X) are used for Hg.

Equation (a) is the reverse of symmetrization and is a redistribution equilibrium of organometallic salts. However, the equilibrium lies far to the right for Zn, Cd or Hg compounds and hence is suitable for the preparation of such monoorganometallic compounds as RMX (M = Zn, Cd or Hg) from 1 : 1 R<sub>2</sub>M and MX<sub>2</sub> (see Table 1 for Hg).

(i) Zinc. The salts used for the Zn reactions are the halides (chlorides, bromides and iodides); both alkyl and aryl compounds are used. Owing to the reactivity of organozinc compounds, air and moisture must be excluded from the reaction. Use of ether or dioxane, on evaporation of the solvent, leads<sup>30,31</sup> to solvates RZnX·D (X = halide, D = Et<sub>2</sub>O or dioxane). The exchange between Et<sub>2</sub>Zn and ZnI<sub>2</sub> occurs<sup>32</sup> slowly in ether at RT.

Exchange between ZnX<sub>2</sub> and R<sub>2</sub>Zn, occurs without a solvent on heating. If R<sub>2</sub>Zn is sufficiently volatile, xs may be used. At the completion of the reaction, the xs R<sub>2</sub>Zn can be removed on heating in vacuo and the residue recrystallized from a solvent, e.g., pentane for EtZnX (X = Cl, Br or I)<sup>33</sup>:



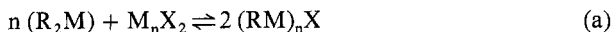
(ii) Cadmium. Ethers are also the preferred solvents for Cd. However, the poor solubilities of Cd halides, in particular CdCl<sub>2</sub> and CdBr<sub>2</sub>, result in slower reactions than found for analogous Zn systems. Long reaction times with vigorous stirring are necessary<sup>34,35</sup>. The reactivity sequence for CdX<sub>2</sub> is CdI<sub>2</sub> > CdBr<sub>2</sub> > CdCl<sub>2</sub> at RT in

270      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
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**5.7.2.3.2. by Redistribution with the Organometallics of the Same Metal.**

Reactions of diorganometal compounds with salts of the metals, e.g.:

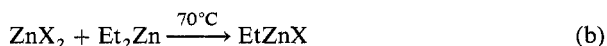


are used to prepare monoorganometallic derivatives<sup>1,2</sup> of Zn, Cd or Hg. In addition to salts of monobasic acids, HX, salts of di- and tribasic acids (H<sub>2</sub>X and H<sub>3</sub>X) are used for Hg.

Equation (a) is the reverse of symmetrization and is a redistribution equilibrium of organometallic salts. However, the equilibrium lies far to the right for Zn, Cd or Hg compounds and hence is suitable for the preparation of such monoorganometallic compounds as RMX (M = Zn, Cd or Hg) from 1:1 R<sub>2</sub>M and MX<sub>2</sub> (see Table 1 for Hg).

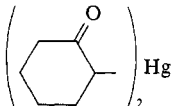
(i) Zinc. The salts used for the Zn reactions are the halides (chlorides, bromides and iodides); both alkyl and aryl compounds are used. Owing to the reactivity of organozinc compounds, air and moisture must be excluded from the reaction. Use of ether or dioxane, on evaporation of the solvent, leads<sup>30,31</sup> to solvates RZnX·D (X = halide, D = Et<sub>2</sub>O or dioxane). The exchange between Et<sub>2</sub>Zn and ZnI<sub>2</sub> occurs<sup>32</sup> slowly in ether at RT.

Exchange between ZnX<sub>2</sub> and R<sub>2</sub>Zn, occurs without a solvent on heating. If R<sub>2</sub>Zn is sufficiently volatile, xs may be used. At the completion of the reaction, the xs R<sub>2</sub>Zn can be removed on heating in vacuo and the residue recrystallized from a solvent, e.g., pentane for EtZnX (X = Cl, Br or I)<sup>33</sup>:



(ii) Cadmium. Ethers are also the preferred solvents for Cd. However, the poor solubilities of Cd halides, in particular CdCl<sub>2</sub> and CdBr<sub>2</sub>, result in slower reactions than found for analogous Zn systems. Long reaction times with vigorous stirring are necessary<sup>34,35</sup>. The reactivity sequence for CdX<sub>2</sub> is CdI<sub>2</sub> > CdBr<sub>2</sub> > CdCl<sub>2</sub> at RT in

TABLE 1. FORMATION OF ORGANOMETAL SALTS,  $(RM)_nX$ , FROM  $R_2M$  AND  $M_nX_2$ :
$$n R_2M + M_nX_2 \rightleftharpoons 2 (RM)_nX$$

$R_2M$	$M_nX_2$	Solvent and conditions	Yield (%)	Ref.
<b>Zinc</b>				
$Et_2Zn$	$ZnI_2$	Dioxane	80	12
$Ph_2Zn$	$ZnBr_2$	$Et_2O$	70	13
$(p-MeC_6H_4)_2Zn$	$ZnCl_2$	$Et_2O$	52	14
	$ZnBr_2$	$Et_2O$	72	15
	$ZnI_2$	$Et_2O$	70	16
$(1-C_{10}H_7)_2Zn$	$ZnCl_2$	$Et_2O$	65	17
<b>Cadmium</b>				
$Et_2Cd$	$CdCl_2$	$Et_2O$ , 10 h, stir	61	18
	$CdBr_2$	$Et_2O$ , 8 h, stir	68	19
$n-Pr_2Cd$	$CdCl_2$	$Et_2O$ , 10 h, stir	44	20
$Ph_2Cd$	$CdI_2$	$Et_2O$ , 3 h, stir	80	21
$(2-thienyl)_2Cd$	$CdI_2$	$Et_2O$ , 9 h, stir	81	22
<b>Mercury</b>				
$Me_2Hg$	$Hg_3(PO_4)_2$	$\Delta$ , $H_2O$	80	23
$(CD_3)_2Hg$	$HgX_2$	—	—	24
	X = Cl, Br or I			25
$Et_2Hg$	$HgCl_2$	95% EtOH	51	26
	$Hg(O_2CCCl_3)_2$	THF, RT	96	27
	$Hg(O_2SPh)_2$	$CHCl_3$	72	3
	$Hg_3(PO_4)_2$	$\Delta$ , trace $H_2O$	98	3
	$Hg_3(AsO_4)_2$	$120^\circ C$ , 1 h	75	3
$[(Me_2Si)_2CH]_2Hg$	$HgBr_2$	EtOH, reflux, 5 h	36	3
$(PhSO_2CH_2)_2Hg$	$HgCl_2$	DMF, $\Delta$ , 3 h	61	3
$(PhCOCH_2)_2Hg$	$HgI_2$	THF	94	
cis-(ClCH=CH) $_2$ Hg	$HgCl_2$	$Et_2O$ , RT	82	4
cis-(PhCOCH=CH) $_2$ Hg	$HgCl_2$	$Et_2O$	65	4
(m-MeO $_2$ CC $_6$ H $_4$ ) $_2$ Hg	$HgBr_2$	EtOH, 2 h, $\Delta$	90	4
$Ph_2Hg$	$Hg(NO_3)_2$	EtOH, $H_2O$ , $HNO_3$	80	5
(o-MeC $_6$ H $_4$ ) $_2$ Hg	$Hg(CNO)_2$	PhH, $80^\circ C$	—	6
$Ph_2Hg$	$Hg(O_2SPh)_2$	$CHCl_3$	80	
(p-MeC $_6$ H $_4$ ) $_2$ Hg	$Hg(O_2SPh)_2$	$CHCl_3$	71	7
$(C_6F_5)_2Hg$	$Hg(N_3)_2$	EtOH	—	8
$(C_6Cl_5)_2Hg$	$HgCl_2$	$PhNO_2$ , 2 h, reflux	90	
$(C_6Br_5)_2Hg$	$HgBr_2$	p-Xylene, $PhNO_2$ , 10 h, $\Delta$	43	9
(o-phenylene-Hg) $_3$	$HgCl_2$	$Me_2CO$ , 8 h, $\Delta$	—	10
$(C_5H_7)_2Hg$	$Hg[N(SiMe_3)_2]$	THF	48	11
$(C_5Cl_7)_2Hg$	$HgCl_2$	PhH, RT	93	7
(o-Me $_2$ NCH $_2$ C $_6$ H $_4$ ) $_2$ Hg	$HgCl_2$	THF, 1 day		7
	$HgCl_2$	THF, 1 h	75	28
$(3,4-Cl_2C_6H_3)_2Hg$	$Hg(OAc)_2$	$MeOH$ , $Me_2CO$ , $100^\circ C$ , 2 h	93	29

$\text{Et}_2\text{O}$ ; times for reaction with  $n\text{-Pr}_2\text{Cd}$  are 2, 10 and 36 h, respectively, for  $\text{CdI}_2$ ,  $\text{CdBr}_2$  and  $\text{CdCl}_2$ . Inert atmospheres, usually  $\text{N}_2$ , are employed. The  $\text{RCdX}$  species are sparingly soluble in ether as in most organic solvents [with the exception of dimethylsulfoxide (DMSO)] and precipitate during the reaction. The precipitate may be washed with  $\text{Et}_2\text{O}$  to remove any trapped  $\text{CdX}_2$  and then dried in vacuo. Unsolvated  $\text{RCdX}$  are obtained from  $\text{Et}_2\text{O}$ .

(iii) Mercury. Not only can the halides be used but so can the nitrate<sup>36</sup>, arenesulfonate<sup>37</sup>, phosphate<sup>38</sup>, arsonate<sup>38</sup>, carboxylates<sup>39-41</sup>, azide<sup>42</sup>, cyanide<sup>43</sup>, cyanate<sup>44</sup> and amides, e.g.<sup>45,46</sup>:

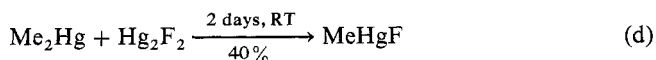


The amides,  $\text{Hg}(\text{NR}'_2)_2$ , include  $\text{R}'_2\text{N} = (\text{Me}_3\text{Si})_2\text{N}$ <sup>45</sup>,  $\text{RCONH}$ <sup>46</sup>, ( $\text{R} = \text{Me}, \text{Et}$  or  $\text{Ph}$ ),  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{NH}$ <sup>47</sup>, and  $\text{PhN}=\text{NNPh}$ <sup>47</sup>. Reactions of  $\text{Hg}(\text{NR}'_2)_2$  with  $\text{Ph}_2\text{Hg}$  are quantitative in such solvents as  $\text{EtOH}$ ,  $\text{N,N}$ -dimethylformamide (DMF) or toluene.

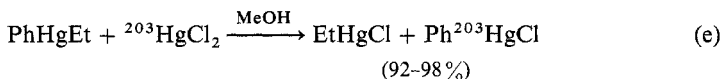
Both monocarboxylates, e.g.,  $\text{Hg}(\text{OCCOCl}_3)_2$ <sup>39</sup> and  $\text{Hg}(\text{OAc})_2$ , where  $\text{OAc}$  is  $-\text{OC}(\text{O})\text{CH}_3$ , and dicarboxylates, e.g.,  $\text{Hg}$  succinate<sup>41</sup> can be used. Chiral carboxylates also are employed. Diastereoisomers are isolated from the reaction of  $s\text{-Bu}_2\text{Hg}$  and the  $\text{Hg}$  salt of the monoethyl ester of (d)-tartaric acid<sup>40</sup>.

The organic groups,  $\text{R}$ , in  $\text{R}_2\text{Hg}$  include simple alkyl, functionally substituted alkyl, aryl, perhaloaryl and alkenyl units. The solvents also cover a wide range (see Table 1). Reactions also are carried out in the absence of solvents, e.g., a solid-state reaction between  $\text{Ph}_2\text{Hg}$  and  $\text{HgCl}_2$  occurs under pressure<sup>47</sup>.

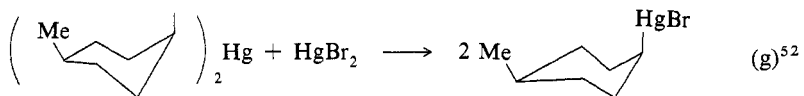
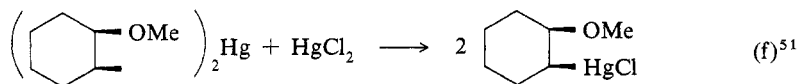
Mercury(I) fluoride also reacts<sup>48</sup> with  $\text{Me}_2\text{Hg}$ :



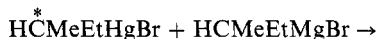
Reactions of unsymmetric compounds,  $\text{RHgR}'$  are known, e.g.<sup>49,50</sup>:



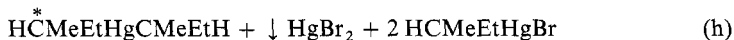
(iv) Stereochemistry. The stereochemistry of exchange for  $\text{Hg}$  systems involves retention of configuration, e.g., for cyclohexyl compounds:



For chiral systems such as <sup>53–55</sup> s-Bu<sub>2</sub>Hg and <sup>56</sup> (t-BuCH<sub>2</sub>CH<sub>2</sub>-CMeH)<sub>2</sub>Hg, cleavage by HgBr<sub>2</sub>, Hg(OAc)<sub>2</sub> or Hg(NO<sub>3</sub>)<sub>2</sub> proceeds with retention. Reactions of HgBr<sub>2</sub> with s-butylmercury, having one racemic and one chiral alkyl group, give half the rotation of the initial chiral s-BuHgBr used to prepare the dialkylmercury, as demanded by a reaction proceeding with retention:



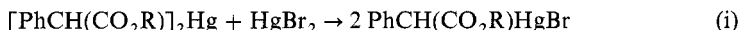
$$[\text{d}]_D^{25} = -19.28$$



$$[\text{d}]_D^{25} = -15.54$$

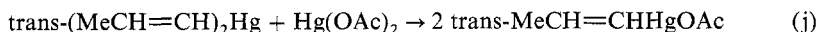
$$[\text{d}]_D^{25} = -9.46$$

Other reactions include that of the (–)-menthyl ester (I)<sup>57</sup>:



(I)

where R = (–)menthyl. 1-Alkenyl groups can be cleaved with retention of configuration, e.g., β-chlorovinyl<sup>58</sup> by HgX<sub>2</sub> (X = Cl or Br) at RT in Et<sub>2</sub>O, and 1-propenyl<sup>59</sup>, by Hg(OAc)<sub>2</sub>:



In contrast to the stereospecific reaction of Hg(OAc)<sub>2</sub>, HgBr<sub>2</sub> provides both cis- and trans-MeCH=CHHgBr products.

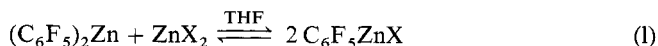
(v) Equilibria. The exchanges are equilibria, but lie far to the right:



where  $K = [\text{RMX}]^2 / [\text{R}_2\text{M}][\text{MX}_2]$ ; e.g., for Me<sub>2</sub>Cd–CdI<sub>2</sub> in tetrahydrofuran (THF)<sup>60</sup> and for R<sub>2</sub>Zn–ZnX<sub>2</sub> (R = Me or Et; X = Cl, Br or I) in THF<sup>61</sup>, values of K are > 100 from spectroscopic data. More precise values are calculated for Me<sub>2</sub>Hg–HgX<sub>2</sub> interactions<sup>62</sup> with  $K = 3.5 \times 10^{11}$ ,  $2.9 \times 10^9$  and  $3.4 \times 10^5$  for X = Cl, Br, or I, respectively.

For some electron-withdrawing R groups, the equilibrium does not lie to the right and equilibrium constants are calculated using polarography, NMR and vibrational spectroscopy.

Equilibrium constants are obtained for C<sub>6</sub>F<sub>5</sub>ZnX:



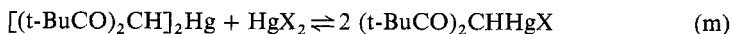
at 35°C these are  $18.1 \pm 5.4$ ,  $16.3 \pm 3.0$  and  $7.5 \pm 0.9$  for X = Cl, Br or I, respectively<sup>63</sup>, in THF. Thermodynamic values for the redistribution equilibrium of C<sub>6</sub>F<sub>5</sub>ZnI in THF are  $\Delta H = 0.88 \pm 0.30 \text{ kJ mol}^{-1}$  and  $\Delta S = 16 \text{ J mol}^{-1} \text{K}^{-1}$ . Values are also solvent dependent, e.g., K for C<sub>6</sub>F<sub>5</sub>ZnI at 35°C =  $30.4 \pm 3.9$ ,  $21.2 \pm 2.7$ ,  $9.1 \pm 0.5$  and  $7.5 \pm 0.9$  in DMSO, DMF, 1,2-dimethoxyethane (DME) and THF, respectively.

TABLE 2. EQUILIBRIUM CONSTANTS FOR  $R_2Hg-Hg(CN)_2$   
 INTERACTIONS<sup>a</sup> IN DMF CONTAINING  $[n-Bu_4N][ClO_4]$ 

$R_2Hg + Hg(CN)_2 \xrightleftharpoons{K} 2 RHgCN$		
R	Temperature (°C)	K
PhC≡C	100	1.1
C <sub>6</sub> F <sub>5</sub>	100	3.6
MeO <sub>2</sub> CCH <sub>2</sub>	100	8.3
	40	3.8
		2.54
		(DMSO)
		0.004 (py)
Ph <sub>2</sub> C=CH	25	> 100

<sup>a</sup> From refs. 43 and 65.

For C<sub>6</sub>F<sub>5</sub>CdI, the values of K are  $3.2 \pm 0.7$  in DMF at  $-40^\circ\text{C}$  and  $3.2 \pm 0.2$  in DMSO at  $35^\circ\text{C}$ ; cf. K = 4 for a statistical constant. Equilibrium constants are also calculated for  $[(t-BuCO)_2CH]_2Hg$ :



$K_{-30^\circ\text{C}} = (6.2 \pm 0.1) \times 10^2$  and  $(1.3 \pm 0.1) \times 10^3$  for X = Cl and OAc, respectively.

The Hg(CN)<sub>2</sub> interactions are also equilibria<sup>43,65</sup>, (see Table 2).

No exchange occurs between<sup>66</sup> (PhC≡C)<sub>2</sub>Hg and HgCl<sub>2</sub> or between<sup>67</sup> [(CF<sub>3</sub>)<sub>2</sub>CF]<sub>2</sub>Hg and HgCl<sub>2</sub> even after 24 h at  $100^\circ\text{C}$ . Although HgBr<sub>2</sub> reacts with (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Hg, HgI<sub>2</sub> does not<sup>68</sup>.

(vi) Rates. Reactions involving cleavage of arylmercury bonds are electrophilic aromatic substitutions. Cleavages of alkylmercury bonds, electrophilic aliphatic substitutions, have S<sub>E</sub>2 mechanisms. One exception is the reaction between (MeOCOCH<sub>2</sub>)<sub>2</sub>Hg and HgCl<sub>2</sub> in DMF which has<sup>69</sup> a mechanism between S<sub>E</sub>1 and S<sub>E</sub>2.

Aryl groups are more readily cleaved from Hg than alkyl [see Eq. (e)].  $\rho$ -Values of  $-5.9$  and  $-4.95$  are found for (p-YC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg and HgI<sub>2</sub> in dioxane<sup>70</sup>. For Ar<sub>2</sub>Hg and Hg(CN)<sub>2</sub> in DMF, respectively<sup>71</sup>. Therefore, electron-releasing groups enhance the rate of exchange.

Only slight reactivity differences are found for dialkyl Hg. Changes in the solvent, temperature and HgX<sub>2</sub> can alter the reactivity sequences; e.g., toward HgI<sub>2</sub> in dioxane, the reactivity is<sup>72</sup> R = (Ph >) cyclo-C<sub>3</sub>H<sub>5</sub> > n-Pr ≈ i-Pr ≈ Et > Me. At  $20^\circ\text{C}$  in MeOH toward HgCl<sub>2</sub>, the sequence is R = Et > n-Pr > cyclo-Pr > Me ≈ i-Pr compared to that toward HgBr<sub>2</sub> of<sup>73</sup> R = Et ≈ n-Pr > i-Pr > Me; at higher T different orders are seen. The sequence toward HgCl<sub>2</sub> in DMF is<sup>69</sup> R = (Ph ≈) CH<sub>2</sub> = CH > > Et > PhCH<sub>2</sub> > C<sub>6</sub>F<sub>5</sub> > MeO<sub>2</sub>CCH<sub>2</sub> > (CF<sub>3</sub>)<sub>2</sub>CH.

The reactivity of Hg salts also is known. Toward s-Bu<sub>2</sub>Hg in EtOH, the sequence is<sup>55</sup> Hg(ClO<sub>4</sub>)<sub>2</sub> > Hg(NO<sub>3</sub>)<sub>2</sub> > Hg(OAc)<sub>2</sub> > HgBr<sub>2</sub>. Pseudohalides have reactivities in the sequence<sup>70</sup> Hg(SCN)<sub>2</sub> > HgI<sub>2</sub> > Hg(CN)<sub>2</sub> toward Ph<sub>2</sub>Hg in dioxane. Sequences for

Hg halides are not so straightforward. The order  $\text{HgCl}_2 > \text{HgBr}_2 > \text{HgI}_2$  holds for reactions of  $\text{Ph}_2\text{Hg}$  in dioxane<sup>70</sup>, for reaction with  $(\text{PhCH}_2)_2\text{Hg}$  in pyridine<sup>74</sup> and for reactions with  $\text{Me}_2\text{Hg}$  in  $\text{MeOH}$ <sup>75</sup>, but toward  $\text{Me}_2\text{Hg}$  in dioxane the reactivity sequence is<sup>48</sup>  $\text{HgBr}_2 > \text{HgCl}_2 > \text{HgI}_2$ .

Solvents, too, affect the rate. The rates increase for Hg reactions  $\text{EtOH} > \text{Me}_2\text{CO}$ <sup>55</sup> and  $\text{EtOH} > \text{PhH} > \text{cyclohexane} > \text{dioxane}$ <sup>70</sup>.

The presence of additional halide ion retards the reaction owing to formation of less-reactive  $[\text{HgX}_3]^-$ . However, the presence of  $\text{Cl}^-$  increases<sup>69</sup> the rate of  $(\text{C}_6\text{F}_5)_2\text{Hg}$  with  $\text{HgCl}_2$ .

(J. L. WARDELL)

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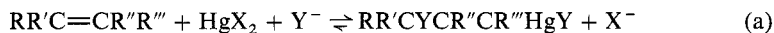
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5.7. Formation of Bonds between Elements of Groups IVB and IIB 277  
 5.7.2. Carbon-Group-IIB Bonds  
 5.7.2.3. from Metal Salts

**5.7.2.3.3. by Addition to Olefins and Acetylenes or Cyclopropanes by Ring Opening.**

(i) With Alkenes. The interaction of an Hg salt<sup>1-6</sup> with an alkene in the presence of a nucleophile can lead to the formation of a  $\beta$ -substituted alkylmercurial:



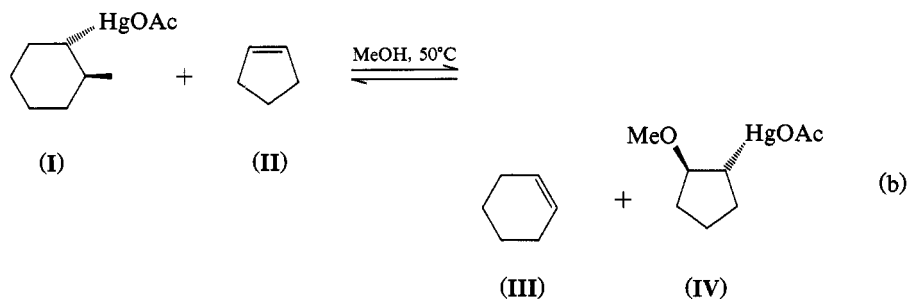
where, e.g.,  $X = OC(O)CH_3$ ,  $OCOCF_3$ ,  $NO_3$ ,  $Cl$ , etc., and  $Y = X$ ,  $OH$ ,  $OR$ ,  $O_2H$ ,  $O_2R$ ,  $NR_2$ ,  $N_3$ ,  $NO_2$ , carbon-bonded anion, etc. (Table 1).

These reactions are solvomercurations when the participating nucleophile is a part of the solvent. The terms oxymercuration for addition of oxygen nucleophiles, aminomercuration for addition of amines, peroxymercuration for addition of  $O_2H$  or  $O_2R$ , etc., are used.

These organomercury reactions are used either to prepare organomercurials or, when combined with subsequent demercuration, as methods to substituted alkanes. Information regarding stereoselectivity and regioselectivity comes from combined oxymercuration-demercuration.

The addition is reversible. Reversion of addition products to the alkenes is also realized on standing as well as on contact with  $KI$ ,  $KCN$ , mineral acids and reagents used for symmetization, e.g.,  $Mg$ .

Trans-oxymercuration also can occur<sup>42</sup>, and equilibria may be set up, e.g.:



where  $K = [III][IV]/[I][II] = 0.3$ . Similar exchanges involving (I) with  $Me_2C=CMe_2$  or norbornene lead to  $K$  values at  $50^\circ C$  in  $MeOH$  of 0.007 and 800, respectively.

In the exchange between chiral (V) and octene, an intermediate complex, involving  $Hg^{2+}$  and both alkenes, is suggested<sup>43</sup> from the induced optical activity in the product,  $n-C_6H_{13}CH(OMe)CH_2HgNO_3$ :

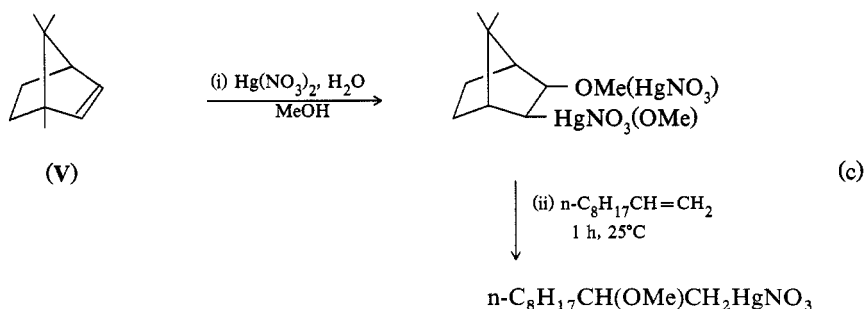
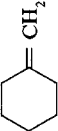
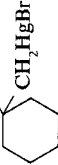
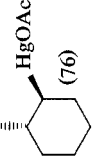
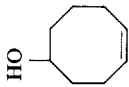
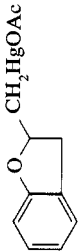
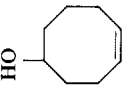
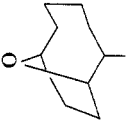
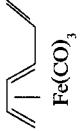
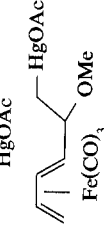
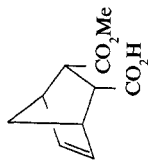
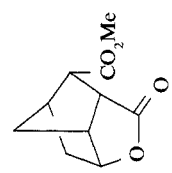
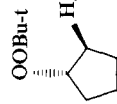
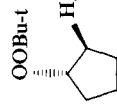
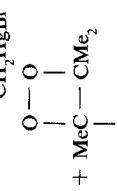
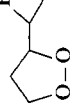


TABLE 1. ADDITIONS TO ALKENES




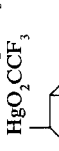
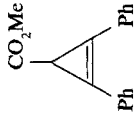
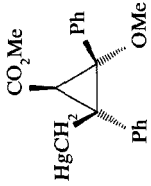
Alkene	Reagents and conditions	Product (yield %)	Ref.
(Z)-PhCMe=CMe-cyclo-C <sub>3</sub> H <sub>5</sub> Cyclopentene	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, THF (i) Hg(OAc) <sub>2</sub> , H <sub>2</sub> O (ii) Cl <sup>-</sup>	PhMeC(HgOAc)CMe(OH)-cyclo-C <sub>3</sub> H <sub>5</sub> trans-2-HO-cyclopentyl HgCl	7
	(i) Hg(OAc) <sub>2</sub> , H <sub>2</sub> O (ii) Br <sup>-</sup>		8
H <sub>2</sub> C=CH <sub>2</sub>	(i) Hg(OAc) <sub>2</sub> , EtOCH <sub>2</sub> CH <sub>2</sub> OH (ii) Cl <sup>-</sup>	EtO(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> HgCl	9
PhCMc=CH <sub>2</sub> Me <sub>3</sub> SiCH=CH <sub>2</sub> cis-MeCH=CHMe	(i) Hg(OAc) <sub>2</sub> , MeOH Hg(OAc) <sub>2</sub> , EtOH Hg(O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> , CD <sub>2</sub> Cl <sub>2</sub> , CD <sub>3</sub> OH, HClO <sub>4</sub>	PhCMc(OMe)CH <sub>2</sub> HgOAc (62) Me <sub>3</sub> SiCH(HgOAc)CH <sub>2</sub> OEt MeCH(OCD <sub>3</sub> )CHMeHg(O <sub>2</sub> CCF <sub>3</sub> ) (64)	10 11 12 13
Cyclohexene	Hg(OAc) <sub>2</sub> , HOAc, 1 h	 (76)	14
2-Allylphenol HO 	Hg(OAc) <sub>2</sub> , THF		15
	Hg(OAc) <sub>2</sub> , THF		16
 Fe(CO) <sub>3</sub>	Hg(OAc) <sub>2</sub> , MeOH		17


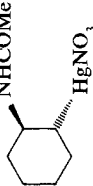
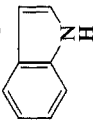
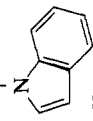


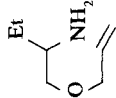
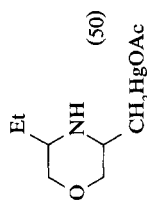

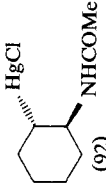
	$\text{Hg}(\text{OAc})_2, \text{MeOH}$		18
$\text{PhCH}=\text{CH}_2$ $\text{PhCMe}=\text{CH}_2$	$\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}_2$ $\text{Hg}(\text{O}_2\text{CCF}_3)_2, \text{CH}_2\text{Cl}_2,$ $\text{H}_2\text{O}_2$ $\text{Hg}(\text{O}_2\text{CCF}_3)_2, t\text{-BuO}_2\text{H},$ $\text{CH}_2\text{Cl}_2$	$\text{PhCH}(\text{O}_2\text{H})\text{CH}_2\text{HgOAc}$ $\text{PhCMe}(\text{O}_2\text{H})\text{CH}_2\text{HgO}_2\text{CCF}_3$ (64) + $[\text{CF}_3\text{CO}_2\text{HgCH}_2\text{CPhMeO}]_2$ (14) $\text{MeCH}(\text{HgO}_2\text{CCF}_3)\text{CHPhO}_2\text{Bu-t}$ (84 parts) + $\text{MeCH}(\text{O}_2\text{Bu-t})\text{-}$ $\text{CHPhHgO}_2\text{CCF}_3$ (16 parts)	19 20
$\text{MeCH}=\text{CHPh}$			21
Cyclopentene	(i) $\text{Hg}(\text{OAc})_2, \text{HClO}_4,$ $t\text{-BuOOH}, \text{CH}_2\text{Cl}_2$ (ii) $\text{Br}^-$		
$\text{CH}_2=\text{CMeCMe}_2\text{O}_2\text{H}$	(i) $\text{Hg}(\text{O}_2\text{CCF}_3)_2, \text{CFCl}_3,$ $-40^\circ\text{C}$	$\text{BrHgCH}_2\text{C}(\text{O}-\text{O})\text{CMe}_2\text{CH}_2\text{HgBr}$ 	22
$\text{HO}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{Me}$	(ii) $\text{Br}^-$	$\text{O}-\text{O}$ $ $ $\text{MeC}-\text{CMe}_2$ $ $ $\text{CH}_2\text{HgBr}$ 	23

(75), one diastereomer

(continued)

TABLE 1. (Continued)

Alkene	Reagents and conditions	Product (yield %)	Ref.
	$\text{Hg}(\text{O}_2\text{CCF}_3)_2, \text{H}_2\text{O}_2$ $\text{CH}_2\text{Cl}_2$		24
	$\text{Hg}(\text{O}_2\text{CCF}_3)_2, \text{H}_2\text{O}_2$ $\text{CH}_2\text{Cl}_2$		25
	(i) $\text{Hg}(\text{O}_2\text{CCF}_3)_2, \text{MeOH}$ (ii) $\text{Cl}^-$		26
$\text{PhCH}=\text{CH}_2$	$\text{PhNH}_2, \text{Hg}(\text{OAc})_2$ $\text{THF}, \text{H}_2\text{O}$	$\text{PhCH}(\text{NHPh})\text{CH}_2\text{HgOAc}$ (51)	27
$\text{PhCH}_2\text{CH}=\text{CH}_2$	$\text{Hg}(\text{NO}_3)_2, \text{PhCH}_2\text{NH}_2$	$\text{PhCH}_2\text{CH}(\text{HgNO}_3)\text{CH}_2\text{NHCH}_2\text{Ph}$ (1 part) + $\text{PhCH}_2\text{CH}(\text{NHCH}_2\text{Ph})\text{CH}_2\text{HgNO}_3$ (9 parts)	28 (71)

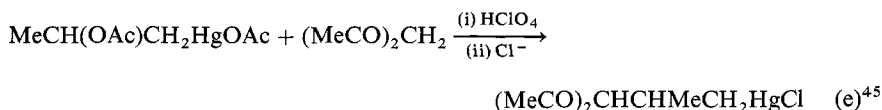
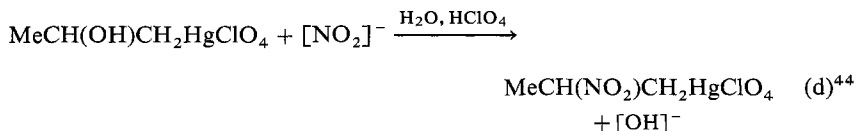
	$\text{Hg}(\text{NO}_3)_2$ , $\text{CH}_2\text{Cl}_2$ , $\text{MeCONH}_2$		29
$\text{PhCH}_2\text{CH}=\text{CH}_2$	(i) $\text{Hg}(\text{NO}_3)_2$ , p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NHNa (ii) KBr	$\text{PhCH}_2\text{CH}(\text{NNaO}_2\text{SC}_6\text{H}_4\text{Me-p})\text{CH}_2\text{HgBr}$	30
$\text{PhNHCH}_2\text{CH}=\text{CH}_2$	(i) $\text{Hg}(\text{OAc})_2$ , $\text{PhNH}_2$ , THF (ii) KBr, H <sub>2</sub> O	$\text{PhNHCH}_2\text{CH}(\text{NHPPh})\text{CH}_2\text{HgBr}$	31
$\text{CH}_2=\text{CHOAc}$	$\text{Hg}(\text{OAc})_2$ 	$\text{AcOHgCH}_2\text{CHOAc}$ 	32
	(i) $\text{Hg}(\text{OAc})_2$ , THF, $\text{PhNH}_2$ (ii) KX		33
	$\text{Hg}(\text{OAc})_2$		34
	(i) $\text{Hg}(\text{NO}_3)_2$ , MeCN (ii) $\text{Cl}^-$ , H <sub>2</sub> O		35
$\text{MeO}_2\text{C}(\text{CH}_2)_8\text{CH}=\text{CH}_2$	(i) $\text{Hg}(\text{NO}_3)_2$ , MeCN (ii) $\text{Cl}^-$ , H <sub>2</sub> O	$\text{CHHgCH}_2\text{CH}(\text{NHCMe})(\text{CH}_2)_8\text{CO}_2\text{Me}$	36

(continued)

TABLE 1. (Continued)

Alkene	Reagents and conditions	Product (yield %)	Ref.
trans-PrCH=CHPr	(i) $\text{Hg}(\text{NO}_3)_2$ , MeCN (ii) $\text{Cl}^-$ , $\text{H}_2\text{O}$	erythro-PrCH(HgCl)- CPrHNHCOMe (65)	36
	$\text{Hg}(\text{OAc})_2$ , $\text{N}_3^-$ , THF, $\text{H}_2\text{O}$		37
	(i) $\text{Hg}(\text{OAc})_2$ , $\text{PhNH}_2$ , THF (ii) KBr	 (100%), (cis:trans = 6.94)	
	(i) $\text{Hg}(\text{OAc})_2$ , $\text{PhNH}_2$ , THF (ii) KBr		38
	$\text{HgCl}_2$ , $\text{PhSO}_2\text{Na}$ , $\text{H}_2\text{O}$ , $\text{Me}_2\text{CO}$ , $20^\circ\text{C}$		39
	$\text{Hg}(\text{OAc})_2$		40
			41

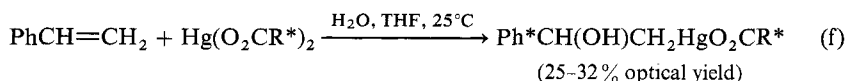
Exchanges of the  $\beta$ -substituents occur, e.g.



(ii) **Mercury Salts.** The most frequently used Hg salt is  $\text{Hg(OAc)}_2$ , whose reactions go completely to the product side. The liberated acetic acid, HOAc, does not react with the oxymercured product, and hence there is no need to remove it. However, for reactions of the more electrophilic and reactive  $\text{Hg(ClO}_4)_2$ , or  $\text{Hg(NO}_3)_2$ , it is necessary to neutralize the liberated acid to prevent decomposition of the addition product and to drive the reaction far over to the product side. The ease of deoxymercuration by HCl limits the use of the weakly electrophilic  $\text{HgCl}_2$ ; however, aminomercurations can be achieved using this salt if sufficient amine is added to act as the base as well as the nucleophile.

Mercury carboxylates other than  $\text{Hg(OAc)}_2$  include  $\text{Hg(OCOCF}_3)_2$ , which is soluble in nonparticipating solvents such as  $\text{CH}_2\text{Cl}_2$  and is a more reactive electrophile than  $\text{Hg(OAc)}_2$ ; in addition,  $[\text{CF}_3\text{CO}_2]^-$  is a poorer nucleophile than  $[\text{AcO}]^-$  and does not take part in addition.

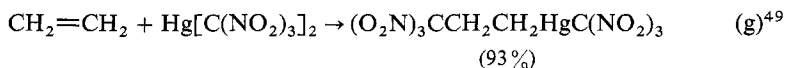
Partial asymmetric synthesis<sup>46,47</sup> is obtained using chiral Hg carboxylates, especially the tartrate:



where  $\text{O}_2\text{CR}^*$  is tartrate.

Other carboxylates, e.g., lactate, 2-phenylpropionate, mandelate and camphorate have a more limited use and success.

Various other Hg salts react; among these salts are  $\text{HgSO}_4$ ,<sup>1</sup> Hg bis(polychlorophenoxides)<sup>1</sup> and the C—Hg-bonded<sup>1,48,49</sup>  $\text{Hg}[\text{C}(\text{NO}_2)_3]_2$ :

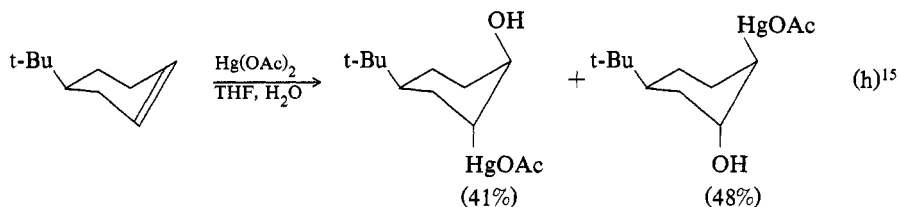


(iii) **Nucleophiles.** The listing of nucleophiles, not exhaustive, given with Eq. (a) indicates how wide ranging is addition: the nucleophile can be a separate entity, including the solvent, or the anionic grouping of  $\text{HgX}_2$  or even a suitably placed center in the alkene. Involvement of the last leads to cyclic products.

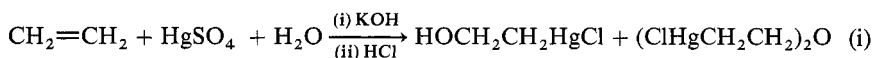
The initial discussion centers on separate nucleophiles and those derived from the Hg salt.

(iv) **Oxygen Nucleophiles.** The most used oxygen nucleophiles are  $\text{H}_2\text{O}$ ; alcohols, in particular MeOH; carboxylates or carboxylic acids;  $\text{H}_2\text{O}_2$  and alkyl hydroperoxides.

Hydroxymercuration is carried out in  $\text{H}_2\text{O}$  or aq tetrahydrofuran (THF), using  $\text{Hg}(\text{OAc})_2$  as the Hg salt, e.g.<sup>1-6</sup>



However, other salts may be used<sup>3</sup>:

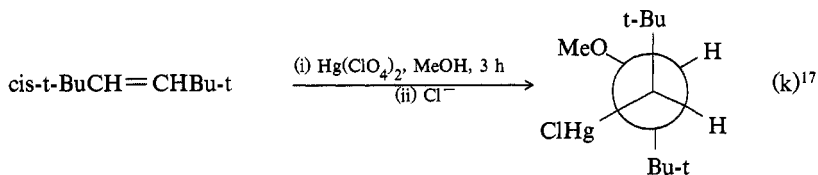


The alcohol formed in Eq. (i) arises by further reaction of the initial product,  $\text{HOCH}_2\text{-CH}_2\text{HgX}$ , with the ethylenemercurinium ion (see later §5.7.2.3.3.viii discussion on intermediates in oxymercuration).

Alkoxymercuration is performed using  $\text{Hg}(\text{OAc})_2$  in the alcohol as solvent. Methanol is used most frequently, and its reactions with an array of alkenes are known:



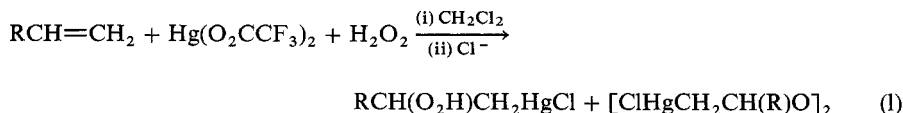
where, e.g.,  $\text{R} = \text{t-Bu}$ ;  $\text{R}' = \text{Me}$ , 100% yield.



Ethanol reacts like<sup>3</sup>  $\text{MeOH}$ ; however, as the nucleophilicity of the alcohol decreases, so the potential for competing acetoxymercuration to provide  $\text{RCH}(\text{OAc})\text{CH}_2\text{HgOAc}$  increases. Such competing reactions become serious when  $\text{t-BuOH}$  is used. Hence, for this and other weakly nucleophilic reagents,  $\text{Hg}(\text{OCOCF}_3)_2$  has advantages<sup>53</sup>, because the  $[\text{CF}_3\text{CO}_2]^-$  ion is too weak a nucleophile to compete with the alkoxide, and so no acyloxymercuration results.

It is also advantageous to use  $\text{Hg}(\text{OCOCF}_3)_2$  rather than  $\text{Hg}(\text{OAc})_2$  for peroxymercuration<sup>54-56</sup>. This is not only to circumvent acyloxymercuration, but to enable the reactions to be carried out with moderate amounts of peroxide.

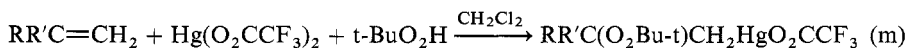
Mixtures of hydroperoxides and di- $\beta$ -mercurioalkylperoxides are obtained<sup>54</sup> from  $\text{H}_2\text{O}_2$ :





where  $R = H, Me$  or  $Ph$ . Such mixtures may be troublesome to separate; however, from  $RMeC=CH_2$  ( $R = Me$  or  $Ph$ ) the hydroperoxide  $RCMeCH(O_2H)CH_2HgCl$  is obtained in  $> 50\%$  yield.

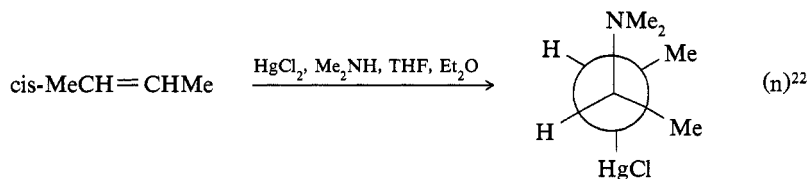
The most popular hydroperoxide in peroxymercuration is  $t-BuO_2H$ , the system used<sup>54,56</sup> frequently with  $Hg(OCOCF_3)_2$  in  $CH_2Cl_2$ :



Acyloxymercuration is carried out in the carboxylic acid media or in nonparticipating media if  $Hg$  carboxylates are used as the electrophile.

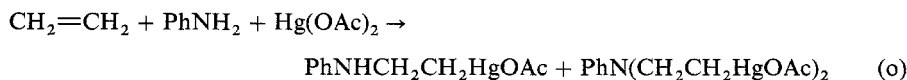
(v) Nitrogen Nucleophiles. Reactive nitrogen nucleophiles include primary or secondary amines,  $[NO_3]^-$ ,  $N_3^-$ , nitriles, amides and sulfonamides.

Aminomercurations of alkenes are known, e.g.<sup>1-6</sup>:

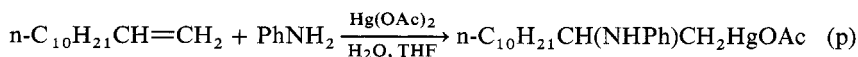


A salt used frequently in aminomercurations is  $HgCl_2$ ; xs amine should also be present to remove the liberated  $HCl$ .

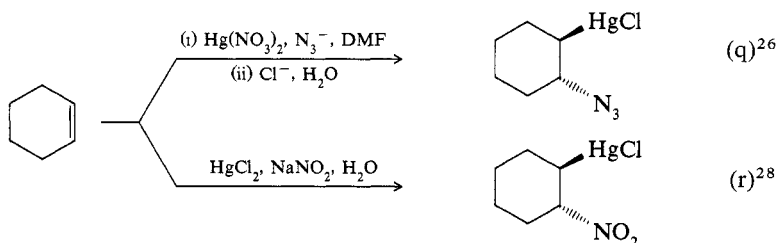
The reaction proceeds for primary and secondary amines; for  $RNH_2$ , both  $NH$  bonds react when  $Hg(OAc)_2$  is used<sup>58</sup>:



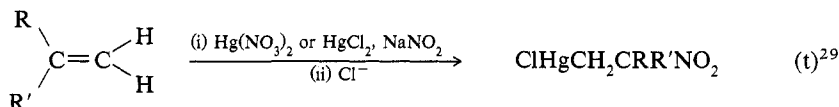
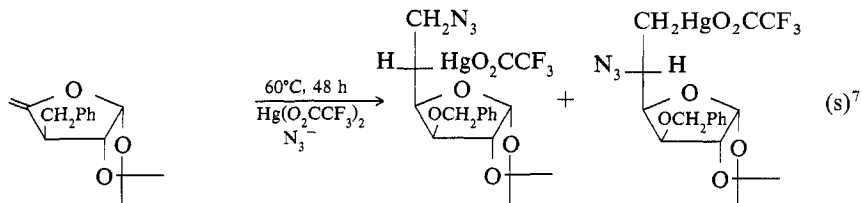
Pressure increases the rates of these sluggish reactions<sup>57</sup>. Reactions in  $H_2O$  also are easier<sup>58</sup>; no accompanying oxymercuration results:



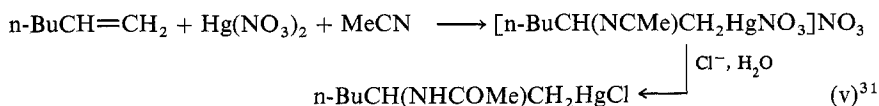
The reactivity of  $HgX_2$  in aminomercurations of  $ArCH_2CH=CH_2$  in  $THF$  is<sup>59</sup>  $X = ClO_4 \approx NO_3 \gg OAc > Cl$ . Amines include alkyl, aryl and substituted amines, e.g.,  $(EtO)_2CHCH_2NH_2$ <sup>59</sup>. Azido-<sup>60,61</sup> and nitromercurations<sup>62,63</sup> occur via standard procedures, e.g.:



where DMF is N,N-dimethylformamide:

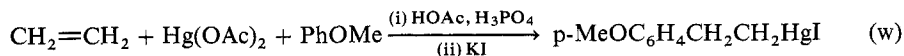


Nitriles, RCN, react with alkenes and Hg salts to provide amide products<sup>30,31</sup>. The reactions proceed in two stages.

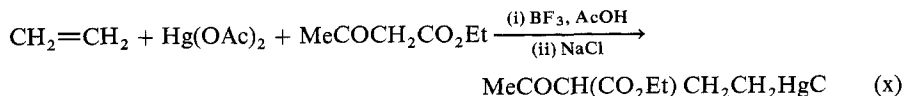


(vi) Other Nucleophiles. Carbon nucleophiles are also active. The use of  $\text{—C(NO}_2)_3$  is illustrated in Eq. (g) in the reaction of  $\text{Hg}[\text{C(NO}_2)_3]_2$  with  $\text{CH}_2=\text{CH}_2$ ;  $\text{Hg}[\text{C(NO}_2)_3]_2$  reacts with other alkenes, including cyclohexene and norbornene<sup>49</sup>.

Other reactive carbon nucleophiles involve<sup>66</sup> PhOMe:

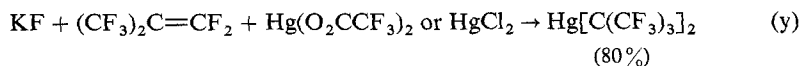


and  $\beta$ -dicarbonyls<sup>67</sup> [see also Eq. (d)]:

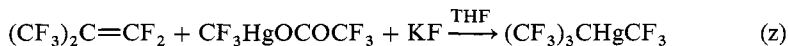


Substituted alkenes, e.g.,  $\text{RCH=CH}_2$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ),  $\text{MeCH=CHMe}$ , cyclohexane, etc., similarly react.

Reactions of  $\text{F}^-$  with perfluoroalkenes in the presence of  $\text{HgCl}_2$  or  $\text{Hg(O}_2\text{CCF}_3)_2$  also arise, e.g.:

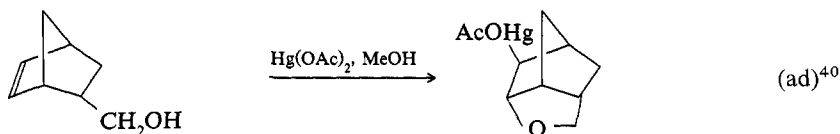
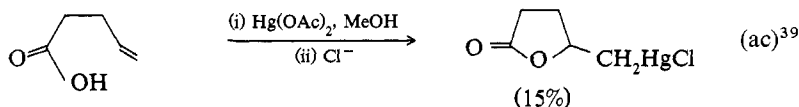
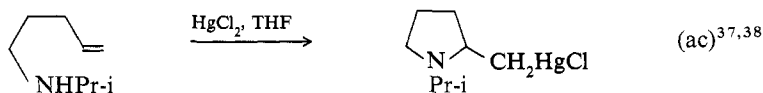
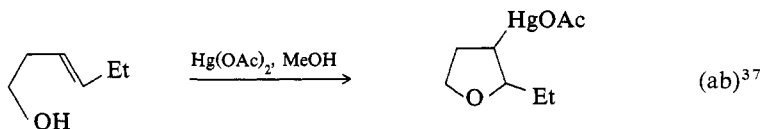


In THF,  $(F_3C)_3CHgCl$  is produced<sup>68</sup> from  $HgCl_2$ ,  $(CF_3)_2C=CF_2$  and  $KF$ . Organo-mercury salts can also take part:

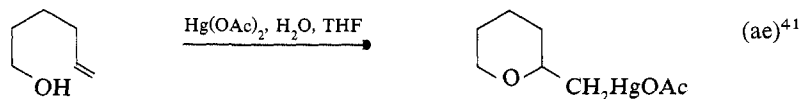


Sulfonylmercuration of conjugated dienes occurs<sup>69</sup> using  $PhSO_2Na$  and  $HgCl_2$ .

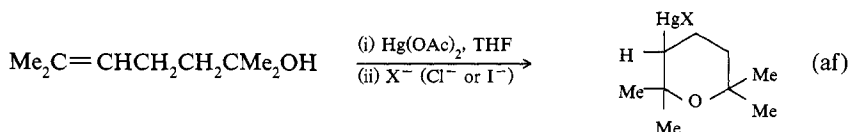
(vii) Intramolecular Nucleophiles. Suitably placed hydroxyl, amine and carboxyl groups in the alkene can act as the nucleophile and give rise to cyclic products. Five-membered rings frequently are formed, e.g.:



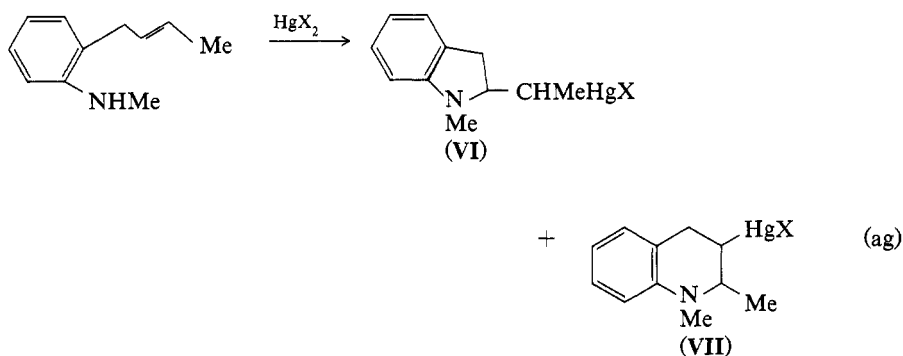
Six-membered rings also are formed, e.g.<sup>41</sup>:



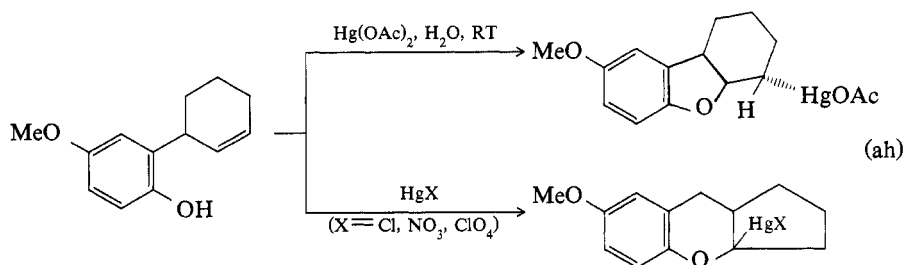
Mercury adds to the carbon atom holding more hydrogens; e.g., the product of  $Me_2C=CHCH_2CH_2CMe_2OH$  is the six-membered ring<sup>42</sup>.



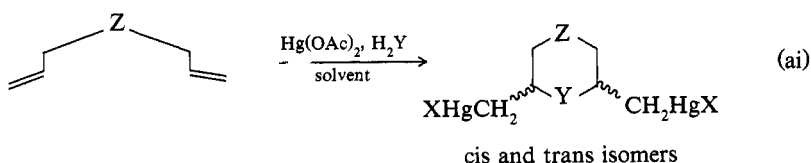
The electrophile and conditions used for the reaction also influence ring size and the products ratio, e.g., (VI):(VII)<sup>37,38</sup>



Another example of the Hg electrophile having an influence on the product of reaction of an alkene<sup>43</sup>:



The more electronegative the anion  $X^-$  in  $HgX_2$ , the more six-membered rings are formed. There is a trans arrangement of the Hg and oxygen atom in each product; i.e., reaction proceeds via intrafacial addition to the  $C=C$  bond. The intramolecular nucleophile can itself be generated from initial reaction of a diene. The eventual product is a bis-mercurated heterocycle, e.g.:

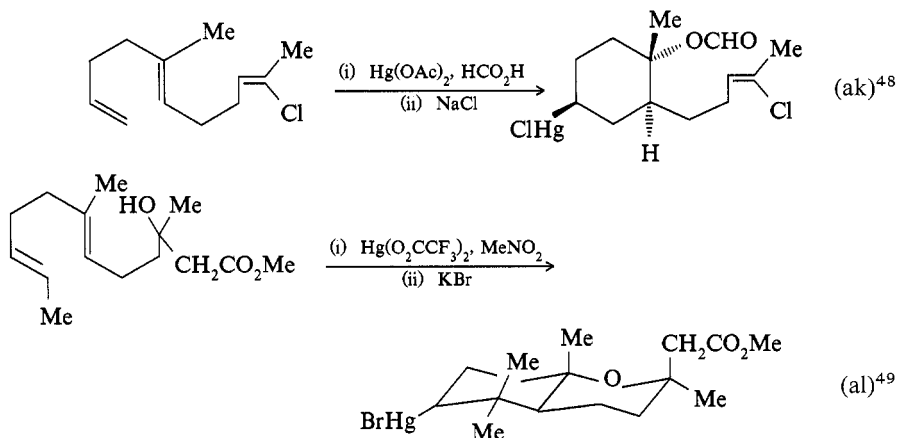


where  $H_2Y = H_2O$ <sup>43</sup>;  $Z = CH_2$ <sup>41</sup>, NH, O or  $S^{44}$ ;  $H_2Y = ArNH_2$  (solvent = THF- $H_2O$ )<sup>44</sup>;  $Z = CH_2$ , NH, O or S;



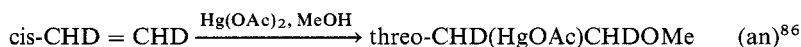
where  $\text{HgX} = \text{Hg}(\text{OAc})_2$ ;  $\text{H}_2\text{Y} = \text{ArNH}_2$  <sup>46</sup> or  $\text{H}_2\text{O}$  <sup>41</sup>;  $\text{HgX}_2 = \text{Hg}(\text{NO}_3)_2$ ;  $\text{H}_2\text{Y} = \text{HOOH}$  (solvent =  $\text{CH}_2\text{Cl}_2$ ) <sup>47</sup>

The internal double bonds of dienes also can act as the initial nucleophilic center <sup>83,84,85</sup>:



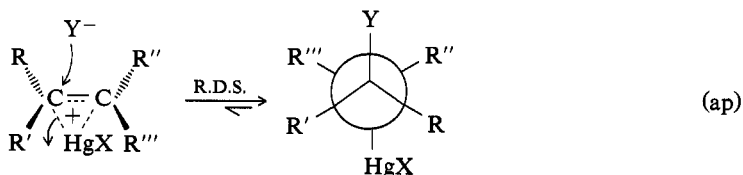
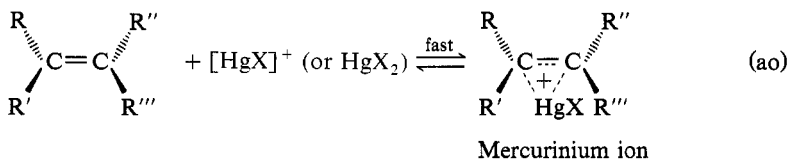
Involvement of another nucleophile—external,  $[\text{HCO}_2]^-$ , as in Eq. (ak) or internal, HO—as in Eq. (al)—is necessary to complete the sequence.

(viii) Mechanism and Stereochemistry. Additions to simple alkenes occur in a trans or an anti manner, e.g., see Eqs. (h), (k) and:



The trans-stereoselectivity is greater than 95% (by NMR) for the reaction of  $t\text{-BuO}_2\text{H}$  and  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  with such alkenes, as  $\text{RCH}=\text{CHR}$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ).

In the addition of the  $[\text{HgX}]^+$  and  $\text{Y}^-$  components [see Eq. (a)] to the alkene, the Hg adds to the carbon holding more hydrogens. The rate law shows a first-order dependence of the alkene and  $\text{Hg}(\text{II})$  species <sup>87,88</sup> and the mechanism for the trans addition to simple alkenes is <sup>89</sup>:

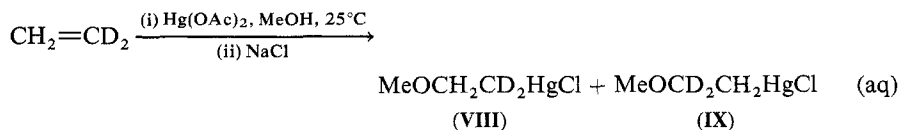


where R.D.S. is the rate-determining step [see Eq. (ap)]. The identity of the active mercurating species<sup>99</sup>, e.g., whether—from Hg(II) acetate—it is  $\text{Hg}(\text{OAc})_2$ ,  $[\text{HgOAc}]^+$ , or even a protonated form when  $\text{HClO}_4$  is also present<sup>86</sup>, is in doubt.

Mercurinium ions [see Eqs. (ao) and (ap)] are too reactive to be detected in the media used for solvo- and oxymercuration but are observed in the gas phase<sup>90-92</sup> and under non-nucleophilic magic-acid<sup>93</sup> conditions. In addition, there is NMR evidence for a cyano-stabilized mercurinium ion in the interaction<sup>94</sup> of  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CN}$  with  $\text{Hg}(\text{NO}_3)_2$  in  $(\text{CD}_3)_2\text{CO}$ .

Despite lack of detection, evidence is available for bridged ions, rather than open  $\beta$ -mercuri-substituted carbonium ions, in addition reactions of simple unstrained alkenes and alkenes not carrying strongly electron-donating substituents. Trans additions, the few rearrangements even for alkenes, such as *cis*-*t*- $\text{BuCH}=\text{CHBu-t}$ , known to undergo carbonium ion rearrangements with other electrophiles and  $\rho$  values point to mercurium ions. The  $\rho$  value of  $-0.9$  for the reaction of  $p\text{-XC}_6\text{H}_4\text{CH}=\text{CHCO}_2\text{Me}$  with  $\text{Hg}(\text{OAc})_2$  in  $\text{MeOH}$  indicates little positive charge on the carbon undergoing nucleophilic attack<sup>87,88</sup>. The  $\rho$  value of  $-3.16$  (or  $\rho^*$  of  $-2.76$ ) for the methoxymercuration of  $p\text{-XC}_6\text{H}_4\text{CH}=\text{CH}_2$  using  $\text{Hg}(\text{OAc})_2$  is too large for a symmetrically bridged ion and too small for an open carbocation<sup>95</sup>, and an unsymmetrically bridged ion intermediate is proposed.

Even for symmetric alkenes such as  $\text{CH}_2=\text{CH}_2$  and *cis*- $\text{MeCH}=\text{CHMe}$ , nonsymmetrically bridged species are proposed. The secondary deuterium isotope effect in the intramolecularly competing methoxymercuration of  $\text{CH}_2=\text{CD}_2$ :



is 1.21 [i.e., (VIII):(IX) = 1.21 : 1]; for (Z)- $\text{MeCD}=\text{CHMe}$  the value is 1.06<sup>96</sup>. This indicates that the transition states for the kinetically controlled reactions have unsymmetric mercurium ion structures in which the two carbons are not equivalent. If an inverse  $\alpha$ -deuterium isotope effect, as found here, indicates a change from  $\text{sp}^2$  to  $\text{sp}^3$  hybridization in the carbon bond, then C—O bond formation occurs in the transition state.

When such strongly resonance-donating substituents as the cyclopropyl group are present, the transition state in the rate-determining step resembles an open carbonium ion<sup>89</sup>.

The order of reactivity in hydroxymercurations of simple alkyl-substituted alkenes<sup>97</sup> is  $\text{R}_2\text{C}=\text{CH}_2 > \text{RCH}=\text{CH}_2 > \text{cis-RCH}=\text{CHR} > \text{trans-RCH}=\text{CHR} > \text{R}_2\text{C}=\text{CHR} > \text{R}_2\text{C}=\text{CR}_2$ , which arises from steric and electronic effects. The reactivity of alkenes is reduced by branching within R or by conjugation of the double bond with an aryl group. The reactivities of alkenes are linked with electronic ( $\sigma^*$ ) and steric ( $\text{E}_s$ ) effects of substituents<sup>98</sup>:

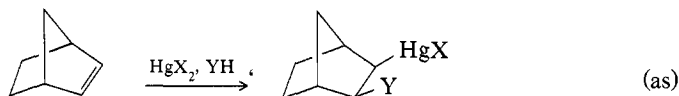
$$\log k = -1.28 - 1.00 \Sigma \sigma^* + 0.91 \Sigma \text{E}_s \quad (\text{ar})$$

That steric hindrance plays a role can be realized, e.g., from the nonreactivity of *trans*-*t*- $\text{BuCH}=\text{CHBu-t}$ , an unstrained but highly hindered alkene, toward  $\text{Hg}(\text{OAc})_2$  in  $\text{MeOH}$ ; *trans*-*t*- $\text{BuCH}=\text{CHBu-t}$  does react, however, with the more powerful  $\text{Hg}(\text{ClO}_4)_2$

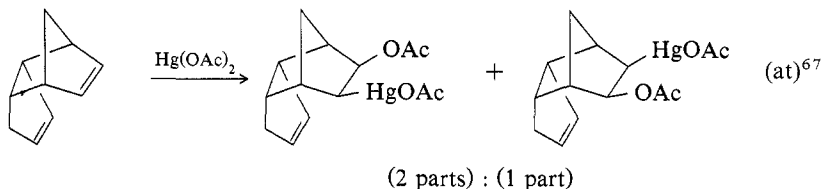
in MeOH to give not the trans adduct, but the cis-addition product<sup>53</sup>, threo-*t*-BuCH(OMe)CH<sub>2</sub>HgClO<sub>4</sub>—the same product as obtained from *cis-t*-BuCH=CHBu-*t*. Although trans or anti addition, without rearrangement, occurs with simple unstrained alkenes, rearrangements or cis additions (e.g., as with *trans-t*-BuCH=CHBu-*t*) are found with more complex and strained alkenes.

Cis additions occur exclusively to *trans*-cyclooctene and *trans*-cyclononane<sup>99</sup>. For these two alkenes, trans addition is hindered. The tendency of an alkene to oxymercuration via a trans mechanism can be related directly to its ability to form the normal anti transition state<sup>99</sup>. If for either steric or twist-strain reasons this transition state is made energetically unfavorable, cis-addition prevails.

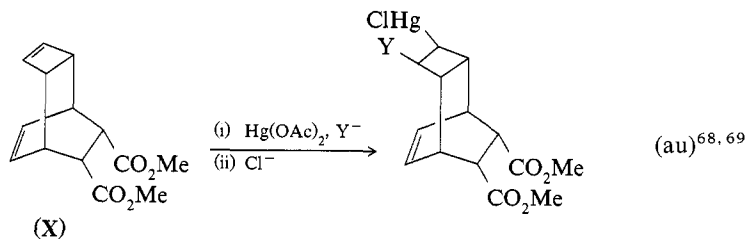
Cis-additions also occur to norbornene<sup>49,58,100–102</sup>, e.g., step (i) in Eq. (c) and:



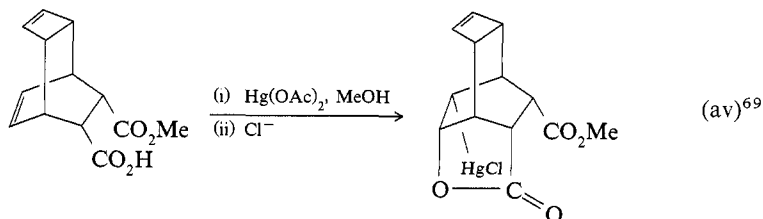
where e.g., HgX<sub>2</sub>, YH = Hg(OAc)<sub>2</sub>, MeOH (+ H<sub>2</sub>SO<sub>4</sub>)<sup>64</sup>, Hg(OCOCF<sub>3</sub>)<sub>2</sub>, *t*-BuO<sub>2</sub>H (in CH<sub>2</sub>Cl<sub>2</sub>)<sup>65</sup>, Hg(OAc)<sub>2</sub>, PhNH<sub>2</sub><sup>24</sup>, Hg[C(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub><sup>14</sup>, Hg(OAc)<sub>2</sub>, N<sub>3</sub><sup>-</sup> (in H<sub>2</sub>O-THF)<sup>66</sup>; norbornadiene<sup>5</sup>, benzonorbornadiene<sup>5</sup>, endo- or exo-bicyclopentadiene<sup>5,67</sup>, e.g.:



bicyclo[3.2.1]octa-2,6-diene<sup>67</sup>, (X)<sup>68,69</sup>



where Y = OH or N<sub>3</sub>;



and cyclopropene<sup>106</sup>.

The products in Eq. (ad)-(av), are the cis-exo adducts. However, for reaction of bicyclo[2.2.2]octadiene with  $\text{Hg}(\text{OAc})_2$  in THF, both cis-exo and cis-endo products are formed<sup>107</sup>:

Reactions (au) and (av) should be contrasted<sup>105</sup>:

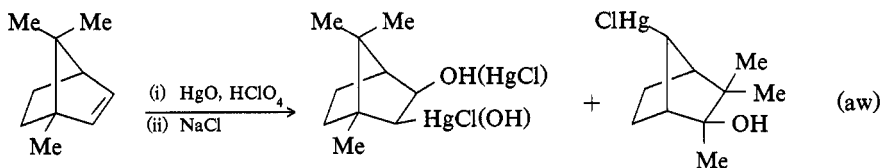
Both trans and cis adducts can be formed in reactions of bicyclo[2.2.2]octene<sup>108,109</sup> and related bicyclooct-2-enes<sup>110</sup>, bicyclo[2.2.2]octadiene<sup>107</sup>, homobarrelenes<sup>107</sup> or dibenzobicyclo[2.2.2]octatrienes<sup>100,111</sup>.

The solvent,  $\text{HgX}_2$ , the nucleophile and even reagent concentrations influence the relative extents of cis : trans addition<sup>100,107,108,111</sup>. Both endo-cis and exo-cis (acetoxymercuration) products are found with homobarrelene and with bicyclo[2.2.2]octadiene with  $\text{Hg}(\text{OAc})_2$  in THF, where also trans-(methoxymercuration) products are obtained<sup>107</sup> in MeOH.

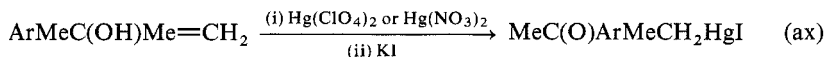
The results for bicyclo[2.2.2]octene derive<sup>108</sup> from the fast reversible formation of mercurium ions, which, if captured rapidly by the solvent, give products of anti addition, but, if attacked only slowly, give products derived from carbonium ions, i.e., rearranged products or syn adducts.

Syn adducts may be formed in a concerted attack on the alkene.

Skeletal rearrangements are rare, but are found for strained bi- and polycyclic alkenes, e.g., bullvalene<sup>112</sup>, bicyclo[4.2.2]deca-2,4,7,9-tetraene<sup>112</sup>, 4,5-exo-trimethylene-2-norbornene<sup>113</sup>, 6-methylenebicyclo[3.1.1]heptane<sup>114</sup>, 5-methylbicyclo[2.1.1]hexene<sup>114</sup>, N-benzyl-9-aza-bicyclo[4.2.2]deca-2,4,7-triene<sup>115</sup>, dibenzobicyclo[2.2.2]octatriene derivatives<sup>111</sup> and bornylene<sup>116</sup>:



Rearrangements also occur with 1-alkylidene-2-alkoxypropanes<sup>117</sup> and with the acyclic  $\text{ArMeC}(\text{OH})\text{CMe}=\text{CH}_2$ <sup>117</sup>:



in reaction with  $\text{Hg}(\text{ClO}_4)_2$  or  $\text{Hg}(\text{NO}_3)_2$ , but not with  $\text{Hg}(\text{OAc})_2$  in MeOH. The latter system provides  $\text{MeArC}(\text{OH})\text{CMe}(\text{OMe})\text{CH}_2\text{HgOAc}$ .

The rate of oxymercuration is not increased when the ground-state strain energy of the alkene is increased. Steric effects and torsional or twist-strain effects in the transition state determine the reactivity<sup>118</sup>.

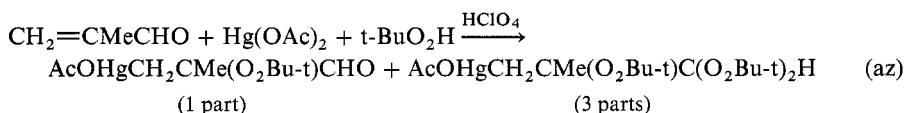
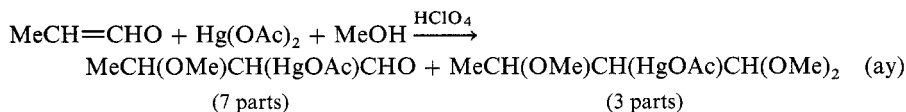
There are distinct patterns of reactivities in brominations and oxymercuration of alkenes. However, the reactivities of the alkenes appear identical when the differences between the steric effects in the transition states for brominations and oxymercuration are taken into account<sup>119</sup>.

(ix) Additions to Substituted Alkenes. Many functional substituents at the double bond can be tolerated, including  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{R}$ ,  $\text{COR}$  or  $\text{CN}$ . These electron-withdrawing groups reduce the reactivity of the alkenes.

Oxymercuration of  $\alpha,\beta$ -unsaturated esters<sup>120</sup>, ketones<sup>120</sup> or aldehydes<sup>121</sup> are regiospecific. Mercury attaches to the  $\beta$ -carbon of  $\text{CH}_2=\text{CRCOMe}$ , i.e., to give



AcOHgCH<sub>2</sub>CROME in methoxymercurations using Hg(OAc)<sub>2</sub> in MeOH; however, with all other substituted  $\alpha,\beta$ -unsaturated carbonyls, the site of mercuration is the  $\alpha$ -carbon. For  $\alpha,\beta$ -unsaturated aldehydes, acetals may be formed also<sup>121</sup>:

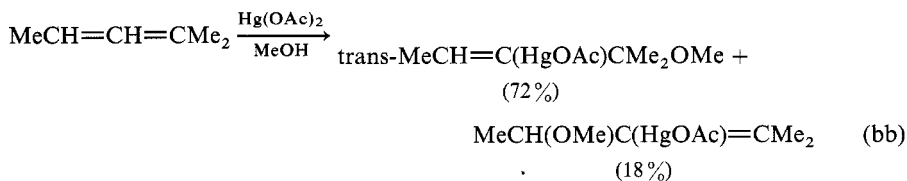


Stereospecific trans addition occurs to  $\alpha,\beta$ -unsaturated esters<sup>87,88</sup>, e.g., cis- or trans-PhCH=CHCO<sub>2</sub>Me; however, either cis- or trans-PhCH=CHCOR provides the same diastereoisomeric mixture of methoxymercurials owing to equilibrium of the diastereoisomers under the reaction conditions.

Addition to alkenyl halides, ethers or acetates also results, but subsequent eliminations in H<sub>2</sub>O can occur<sup>3</sup>. Allene can give terminally bis-oxymercured products<sup>122</sup>, e.g.:

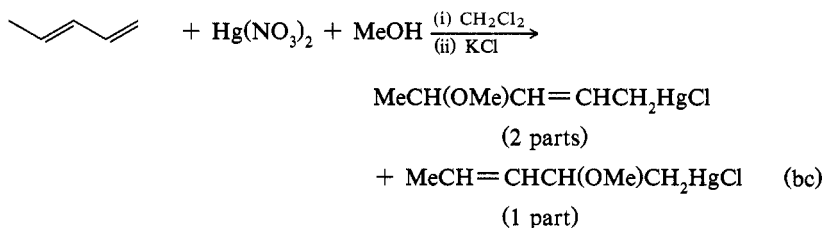


In contrast, substituted allenes provide the centrally mercured product:

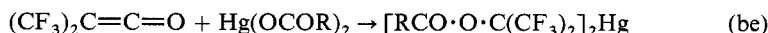
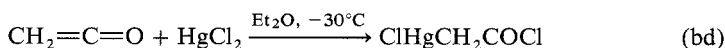


Only monoaminomercuration<sup>123</sup> of Me<sub>2</sub>C=C=CH<sub>2</sub> occurs, using PhNH<sub>2</sub> and Hg(OAc)<sub>2</sub> in aq THF, to give CH<sub>2</sub>=C(HgOAc)CMe<sub>2</sub>NHPh.

Both 1,2- and 1,4-oxymercations occur<sup>124</sup> with MeCH=CHCH=CH<sub>2</sub>:

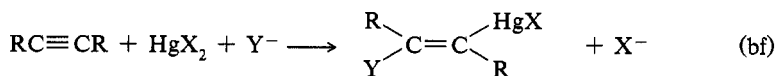


Addition to ketenes also results<sup>125,126</sup>:



where R = Ph, Me or CF<sub>3</sub>.

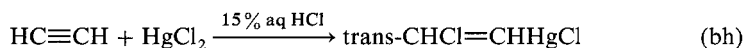
(x) With Alkynes<sup>127</sup>. The reaction of  $\text{HgX}_2$  and  $\text{Y}^-$  with alkynes is a route to alkenylmercurials:



A second addition to give  $\text{RCY}_2\text{CR}(\text{HgX})_2$  also may result. When the nucleophile is  $\text{H}_2\text{O}$  or  $[\text{OH}]^-$ , the initial product may rearrange to a carbonyl compound (i.e., may ketonize):

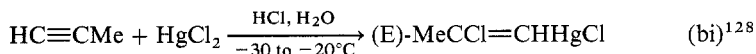


Mercuration is possible for terminal alkynes (see §5.7.2.3.4). Addition by  $\text{HgCl}_2$  to  $\text{HC}\equiv\text{CH}$  occurs under acidic conditions to give the trans-adduct, trans- $\text{CHCl}=\text{CHHgCl}$ :

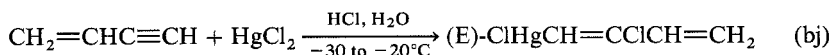


The cis-isomer is obtained from  $\text{HgCl}_2$  with  $\text{HC}\equiv\text{CH}$  (vapor)<sup>1</sup> at  $100^\circ\text{--}110^\circ\text{C}$ .

Other terminal alkynes reacting with  $\text{HgCl}_2$  in acid include<sup>127</sup>  $\text{HC}\equiv\text{CMe}$ :

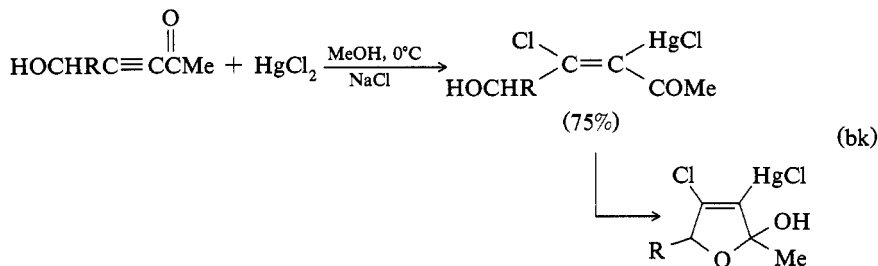


$\text{CH}_2=\text{CHC}\equiv\text{CH}$ :



and  $\text{R}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$ <sup>1,3,127</sup>. In the presence of  $[\text{SCN}]^-$ , the product<sup>129</sup> of  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$  or  $\text{SCN}$ ) with  $\text{RC}\equiv\text{CH}$  is (E)- $\text{RC}(\text{SCN})=\text{CHHgX}$ ; similar additions to internal alkynes also occur.

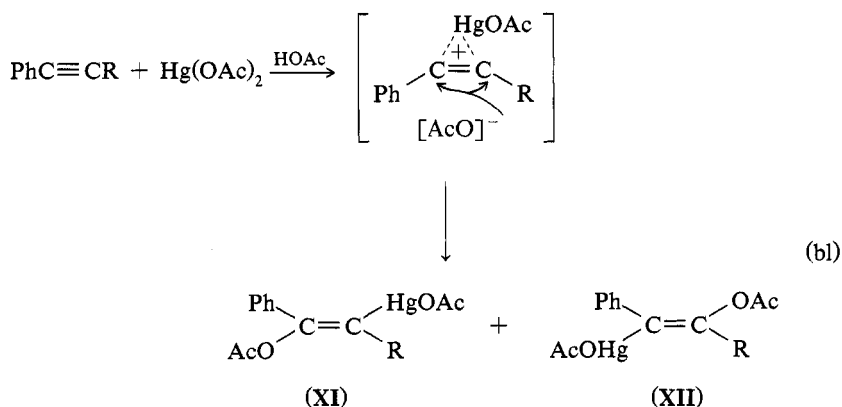
Functionally substituted alkynes<sup>127</sup>, e.g.,  $\text{RC}\equiv\text{CY}$  ( $\text{Y} = \text{CO}_2\text{R}$ <sup>130</sup> or  $\text{OR}'$ <sup>131</sup>), also react with  $\text{HgCl}_2$  to give  $\text{RCCl}=\text{CYHgCl}$ . cis-Addition of  $\text{HgCl}_2$  occur to certain 4-hydroxy-2-alkyn-1-ones, e.g.<sup>127</sup>:



where R = H or Me. Additions to  $\text{HOCH}_2\text{C}\equiv\text{CCO}_2\text{Me}$  and to  $\text{HOCMe}_2\text{C}\equiv\text{CCOMe}$ , on the other hand, proceed via the more normal trans mode<sup>127</sup>, to give (E)- $\text{HOCH}_2\text{CCl}=\text{C}(\text{CO}_2\text{Me})\text{HgCl}$  and (E)- $\text{HOCMe}_2\text{CCl}=\text{C}(\text{COMe})\text{HgCl}$ , respectively.

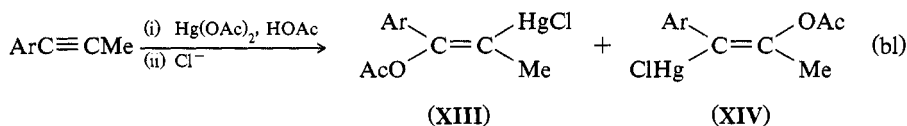
Simple internal aliphatic alkynes afford both regio- and stereochemical mixtures of alkenylmercurials, with the trans adducts predominating<sup>127</sup>. At RT, trans-addition of  $\text{Hg}(\text{OAc})_2$  occurs to  $\text{MeC}\equiv\text{CMe}$  in  $\text{AcOH}$ ; however, on heating, the cis-adduct is obtained<sup>132</sup>.

Complete trans-addition occurs in the acetoxymercuration of  $\text{PhC}\equiv\text{CR}$ , but not regiospecifically<sup>8,134</sup>:



The ratio of the two products depends on the size of R; [XI]:[XII] varies from 3 for R = Me to 16.5 for R = Bu-n. The intermediate has a bridged structure with bent-back groups (Ph and R) which hinder the incoming  $[\text{OAc}]^-$  group [Eq. (bk)]. No addition occurs to the hindered  $\text{PhC}\equiv\text{CBu-t}$ , and only cis addition results with  $\text{PhC}\equiv\text{CPr-i}$  to give (E)- $\text{PhC}(\text{HgOAc})=\text{C}(\text{OAc})\text{Pr-i}$ .

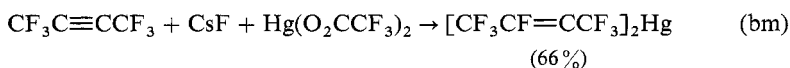
The regioselectivity of the addition to  $\text{ArC}\equiv\text{CMe}$  depends on the substituents in the aryl group<sup>135</sup>:



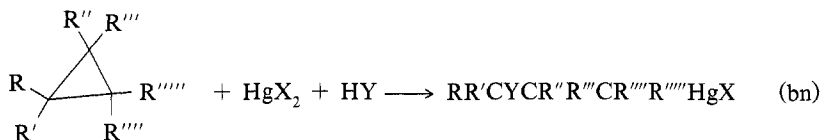
Some values of [XIII]:[XIV] are 1.1:1 (Ar = m- $\text{ClC}_6\text{H}_4$ ), 2.85:1 (Ph), 14:1 (p- $\text{MeC}_6\text{H}_4$ ) and 100:0 (p- $\text{MeOC}_6\text{H}_4$ ). For  $\text{PhC}\equiv\text{CPh}$  only cis-addition results<sup>135,136</sup>; the more usual trans-addition occurs to 3-hexyne<sup>136</sup>.

Arylaminomercuration of terminal alkynes occurs<sup>137</sup>.

Reaction also occurs<sup>138</sup> between perfluoroalkynes,  $\text{F}^-$  and  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ , e.g.:

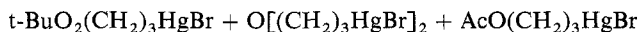
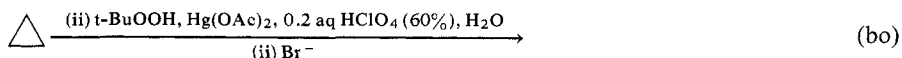


(xi) With Cyclopropanes: Ring-Opened Products. Such reactions lead to  $\gamma$ -substituted products:

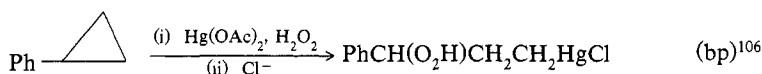
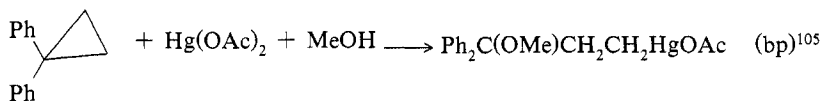


Cyclopropanes are less reactive than alkenes; retroaddition also occurs less readily, and cyclopropane adducts have a high acid tolerance. The nucleophiles that react include OH, OR, OCOR, O<sub>2</sub>H, O<sub>2</sub>R and RCN.

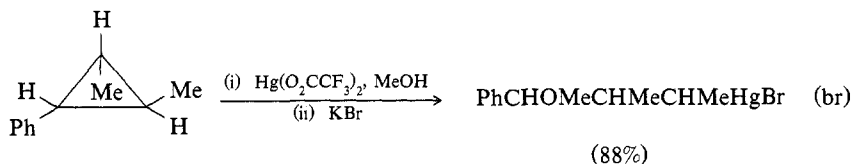
Unsubstituted cyclopropane undergoes<sup>139</sup> a slow reaction with Hg(OAc)<sub>2</sub> and t-BuOOH in CH<sub>2</sub>Cl<sub>2</sub>:



In the ring opening if one of the carbons bears no substituent, then the Hg becomes attached to it and the nucleophile adds to the carbon best able to support a positive charge, e.g.:



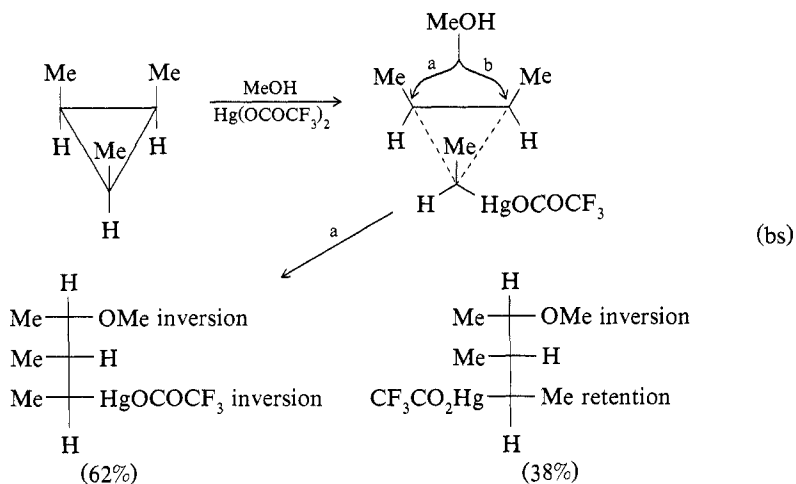
When all three carbons in the ring carry substituents, the addition is still regiospecific<sup>142</sup>. The Hg attacks the least substituted bond or for bonds of equal substitution, at the cis-substituted rather than the trans-substituted bond, with the nucleophile again becoming attached to the site best able to support a positive charge.



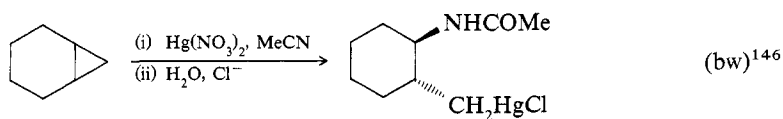
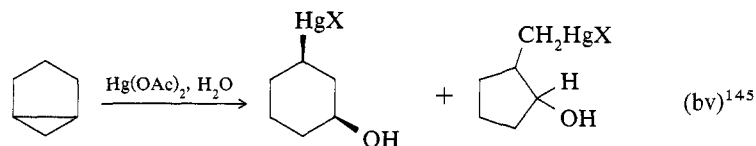
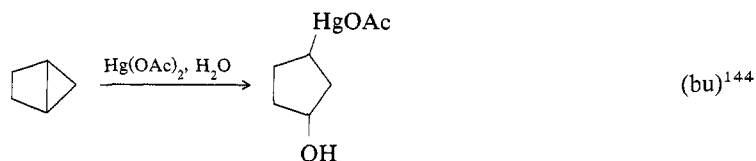
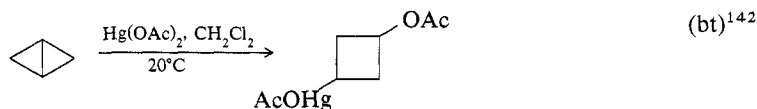
The stereoselectivity is high. For unsymmetrically substituted cyclopropanes, electrophilic attack by the Hg(II) species can occur with predominant retention or inversion, but there is always inversion of configuration at the site of nucleophilic attack<sup>142</sup>.

In symmetrical cis,cis-1,2,3-trimethylcyclopropane more inversion occurs at the site of mercuration, whereas nucleophilic attack by MeOH proceeds with 100% inversion. A

corner-mercured intermediate is possible:



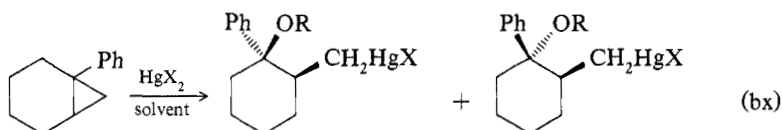
As well as monocyclic cyclopropanes, bi- and polycyclic compounds containing three-membered rings react, e.g.:



Ring strain in the smaller bicyclic compounds leads to adducts from the addition of Hg to the carbon atom holding fewer hydrogens<sup>142-144</sup>. For the larger bicyclo[3.1.0]-heptane exclusive attack of Hg at the carbon holding more hydrogen, results<sup>146</sup> in the

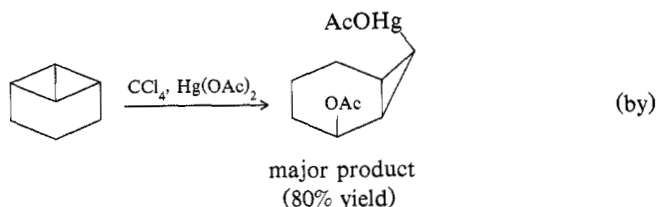
*trans*-adduct; i.e., the nucleophile attacks with 100% inversion. With 1,1-dimethylbicyclo[3.1.0]heptane the electrophile [e.g.,  $\text{Hg}(\text{OAc})_2$  in MeOH] attacks with inversion of configuration<sup>147</sup>.

The stereochemistry of ring opening of 1-phenylbicyclo[3.1.0]heptane (1-phenylnorcarane) depends on the electrophile and solvent<sup>148</sup>:

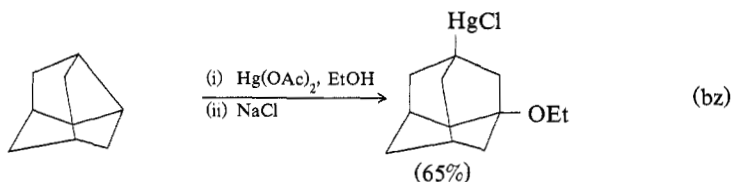


where the product ratios are 13.5:86.5 for  $\text{Hg}(\text{OAc})_2\text{-H}_2\text{O}$  and 69.5:30.5 for  $\text{Hg}(\text{OCOCF}_3)_2$  in cyclohexane.

Solvent also influences the products of reaction of tricyclo[3.1.1.0<sup>6,7</sup>]heptane<sup>147</sup>. In contrast to the reaction with  $\text{Hg}(\text{OAc})_2$  in  $\text{CCl}_4$  the major product with  $\text{Hg}(\text{OAc})_2$  in MeOH is formed by cleavage of the central zero bridge:



An adamantyl derivative is prepared by ring opening<sup>150</sup>:



(J. L. WARDELL)

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302      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
           5.7.2. Carbon-Group-IIB Bonds  
           5.7.2.3. from Metal Salts

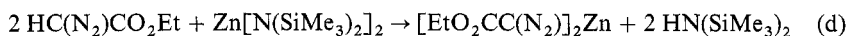
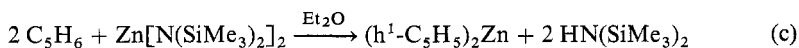
**5.7.2.3.4. with Acidic Hydrocarbons.**

Reaction of Zn, Cd or Hg salts with organic compounds containing acidic hydrogens can lead to the formation of organometallic derivatives on substitution of hydrogen(s) by the metal:

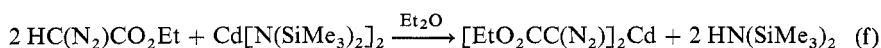
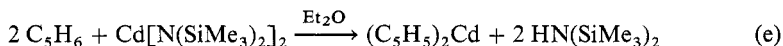


These electrophilic substitutions are used most extensively for Hg. As well as aliphatics, aromatics react with Hg salts.

(i) Metallation of Aliphatics by Zinc. The basic Zn amide,  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ , reacts with cyclopentadiene<sup>1</sup> and with the diazoester<sup>2</sup>,  $\text{HC}(\text{N}_2)\text{CO}_2\text{Et}$  to give diorganozinc products:



(ii) Metallation of Aliphatics by Cadmium. The Cd amide,  $\text{Cd}[\text{N}(\text{SiMe}_3)_2]_2$ , reacts<sup>1,2</sup> like  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ :



Cadmium oxide metallates<sup>3</sup> 1,3-ketones:



However,  $\text{CH}_2(\text{CO}_2\text{Et})_2$ ,  $\text{NCCH}_2\text{CO}_2\text{Et}$  and  $\text{CH}_2(\text{CN})_2$  are unaffected even in refluxing toluene<sup>3</sup>. Cadmium chloride is unreactive.

(iii) Metallation of Aliphatics by Mercury. More acidic hydrocarbons can be metallated by Hg salts<sup>4,5</sup> than by Zn or Cd; e.g., terminal alkynes<sup>6-9</sup>, alkenes<sup>10-13</sup>, cyclopentadienes<sup>14-17</sup> and compounds containing such electron-withdrawing groups as carbonyl<sup>18,19</sup>, cyano<sup>20,21</sup>, nitro<sup>22,23</sup>, chloro<sup>24</sup>, fluoro<sup>25</sup>, diazo<sup>26-29</sup>, sulfonyl<sup>30</sup> and phosphoryl<sup>31</sup>—all groups that render the  $\alpha$  hydrogens acidic (Table 1). Compounds bearing one of these groups are sufficiently acidic to react with Hg salts, but two or more such groups, including combinations of different groups, may be necessary. Extra groups further enhance the acidity of the  $\alpha$  hydrogens, thereby enabling more facile reactions.

Several Hg salts are employed; although Hg halides, acetate and even  $\text{Hg}[\text{C}(\text{NO}_2)_3]_2$  are utilized, HgO and  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$  are particularly useful. The amide,  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$ , e.g., reacts<sup>34</sup> with  $\text{PhCH}_2\text{CN}$  ( $\text{pK}_a$  22.2),  $\text{PhCOMe}$  ( $\text{pK}_a$  24.7),  $\text{Me}_2\text{CO}$  ( $\text{pK}_a$  26.5) and  $\text{PhC}\equiv\text{CH}$  ( $\text{pK}_a$  28.5), but not the less acidic  $\text{MeCN}$  ( $\text{pK}_a$  31.3), to give salt-free diorganomercurials, reaction occurring at the most acidic site, e.g.:

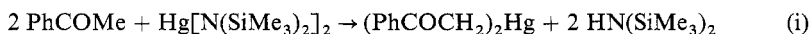
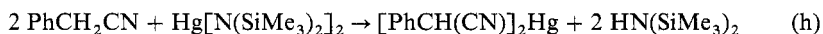
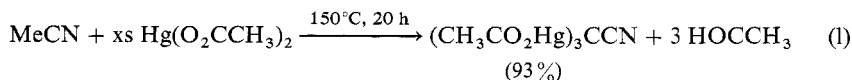


TABLE 1. MERCURATION OF ACIDIC HYDROCARBONS

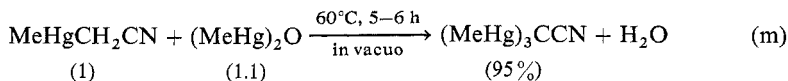
Compound	Condition for mercuration	Product (yield, %)	Ref.
Me <sub>3</sub> SiC≡CH	Hg(OAc) <sub>2</sub> , MeOH	Me <sub>3</sub> SiC≡CHgOAc (72)	6
MeC≡CH	Hgl <sub>2</sub> , NaOH	(MeC≡C) <sub>2</sub> Hg	9
PhC≡CH	HgCl <sub>2</sub> , Et <sub>3</sub> N, H <sub>2</sub> O	(PhC≡C) <sub>2</sub> Hg (94)	7
HC≡CH	MeHgCl, NaOH	MeHgC≡CHgMe (> 80)	32
MeC≡CC≡CH	Hgl <sub>2</sub> , KI, KOH, EtOH	(MeC≡CC≡C) <sub>2</sub> Hg (30)	8
Cl <sub>2</sub> C=CHCl	Hg(CN) <sub>2</sub> , KOH, H <sub>2</sub> O, 36 h	(Cl <sub>2</sub> C=CCl) <sub>2</sub> Hg (86)	12
(p-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> C=CH <sub>2</sub>	(i) Hg(OCOCF <sub>3</sub> ) <sub>2</sub> , F <sub>3</sub> B·OMe <sub>2</sub> , Et <sub>2</sub> O (ii) NaCl	(p-MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> C=CHHgCl (90)	13
(p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> C=CH <sub>2</sub>	(i) Hg(NO <sub>3</sub> ) <sub>2</sub> , MeOH (ii) NaCl	(p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> C=C(HgCl) <sub>2</sub> (54)	13
C <sub>5</sub> H <sub>6</sub>	HgO, i-PrNH <sub>2</sub>	(C <sub>5</sub> H <sub>7</sub> ) <sub>2</sub> Hg (> 85)	14
	Hg[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	(C <sub>5</sub> H <sub>7</sub> ) <sub>2</sub> Hg (97)	58
MeCOMe	(i) HgO, Hg(NO <sub>3</sub> ) <sub>2</sub> , CaO (iii) KI	MeCOCH <sub>2</sub> HgI (78)	18
CH <sub>2</sub> (CO <sub>2</sub> Me) <sub>2</sub>	HgO, H <sub>2</sub> O	[(MeO <sub>2</sub> C) <sub>2</sub> CH] <sub>2</sub> Hg (71)	39
(t-BuCO) <sub>2</sub> CH <sub>2</sub>	HgCl <sub>2</sub> , EtOH, H <sub>2</sub> O, NaOAc;	(t-BuCO) <sub>2</sub> CHHgCl (27)	38
	HgCl <sub>2</sub> (xs), EtOH, H <sub>2</sub> O, NaOAc;	(t-BuCO) <sub>2</sub> C(HgCl) <sub>2</sub> (50)	38
	Hg(OAc) <sub>2</sub> , EtOH, H <sub>2</sub> O;	(t-BuCO) <sub>2</sub> CHHgOAc (67)	38
	Hg(OAc) <sub>2</sub> , EtOH, H <sub>2</sub> O (0.45 equiv);	[(t-BuCO) <sub>2</sub> CH] <sub>2</sub> Hg (27)	38
	Hg[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> , Et <sub>2</sub> O	[(t-BuCO) <sub>2</sub> CH] <sub>2</sub> Hg (71)	38
CH <sub>2</sub> [P(O)(OEt) <sub>2</sub> ] <sub>2</sub> CO <sub>2</sub> Et	Hg(OAc) <sub>2</sub> , THF	(AcOHg) <sub>2</sub> C[P(O)(OEt) <sub>2</sub> ] <sub>2</sub> CO <sub>2</sub> Et	31
CH <sub>2</sub> [P(O)(OEt) <sub>2</sub> ] <sub>2</sub> C(O)NEt <sub>2</sub>	Hg(NO <sub>3</sub> ) <sub>2</sub> , HNO <sub>3</sub> , H <sub>2</sub> O, hexane, 1 day	Et <sub>2</sub> NCO[(EtO) <sub>2</sub> P(O)]CHHgNO <sub>3</sub>	33
CH <sub>2</sub> (SO <sub>2</sub> Ph) <sub>2</sub>	Hg(OAc) <sub>2</sub> (1 equiv), MeOH	(PhSO <sub>2</sub> ) <sub>2</sub> CHHgOAc (95)	30
	Hg(OAc) <sub>2</sub> (3 equiv), MeOH	(PhSO <sub>2</sub> ) <sub>2</sub> C(HgOAc) <sub>2</sub> (85)	30
HCF(NO <sub>2</sub> ) <sub>2</sub>	HgO, Et <sub>2</sub> O, RT, 48 h	[F(NO <sub>2</sub> ) <sub>2</sub> C] <sub>2</sub> Hg (87)	23
HC(NO <sub>2</sub> ) <sub>3</sub>	HgO, Et <sub>2</sub> O, RT	[(NO <sub>2</sub> ) <sub>2</sub> C] <sub>2</sub> Hg (80)	95
HC(N <sub>2</sub> )CO <sub>2</sub> Me	MeHgCl, EtOH, KOEt, 0°C	MeHgC(N <sub>2</sub> )CO <sub>2</sub> Me (86)	51
HC(N <sub>2</sub> )COBu-t	HgO, petrol ether, RT	Hg[C(N <sub>2</sub> )COBu-t] <sub>2</sub> (81)	48
HCN <sub>2</sub> CO <sub>2</sub> Et	Hg[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> , Et <sub>2</sub> O, -20°C	Hg[C(N <sub>2</sub> )CO <sub>2</sub> Et] <sub>2</sub> (100)	2
HC(N <sub>2</sub> )CF <sub>3</sub>	HgO, 5 h, 0°C	Hg[C(N <sub>2</sub> )CF <sub>3</sub> ] <sub>2</sub> (95)	26
HC(N <sub>2</sub> )P(O)Ph <sub>2</sub>	HgO, CHCl <sub>3</sub>	Hg[C(N <sub>2</sub> )P(O)Ph <sub>2</sub> ] <sub>2</sub> (82)	28
C <sub>5</sub> Cl <sub>5</sub> H	Hg(OMe) <sub>2</sub> , 0°C	(C <sub>5</sub> Cl <sub>5</sub> ) <sub>2</sub> Hg (65)	17
	PhHgOH, Me <sub>2</sub> C(OMe) <sub>2</sub> , C <sub>6</sub> H <sub>14</sub>	PhHgC <sub>5</sub> Cl <sub>5</sub> (34)	17



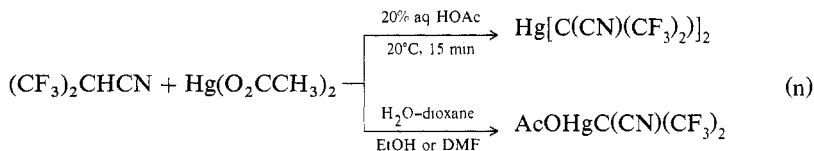
The lack of reaction between Hg[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and MeCN contrasts with the success found for Hg(OCCH<sub>3</sub>)<sub>2</sub>. The reaction between Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> with MeCN can lead to trimercured acetonitrile<sup>20</sup>:



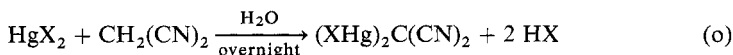
The oxide  $(\text{MeHg})_2\text{O}$  also reacts<sup>21</sup> with  $\text{MeCN}$  (and  $\text{CD}_3\text{CN}$ ) to give  $\text{MeHgCH}_2\text{CN}$  (and  $\text{MeHgCD}_2\text{CN}$ ); further reaction of  $\text{MeHgCN}$  with  $(\text{MeHg})_2\text{O}$  provides  $(\text{MeHg})_3\text{CCN}$ :



The cyanide,  $(\text{CF}_3)_2\text{CHCN}$ , is mercurated by  $\text{Hg}(\text{OAc})_2$ ; either mono- or diorgano-mercurials are obtained depending<sup>25</sup> on the conditions:

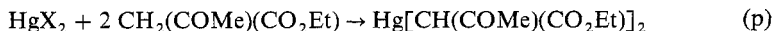


The amide,  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$ , reacts with  $\text{CH}_2(\text{CN})_2$  to give<sup>35</sup>  $\text{Hg}[\text{CH}(\text{CN})_2]_2$ ; but  $\text{HgO}$  is unreactive even in refluxing toluene<sup>36</sup>. Dimetallation of  $\text{CH}_2(\text{CN})_2$  occurs on reaction<sup>36</sup> with  $\text{Hg}(\text{OAc})_2$  or  $\text{HgCl}_2$ :

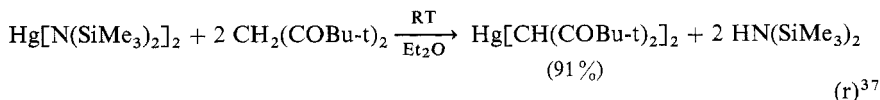
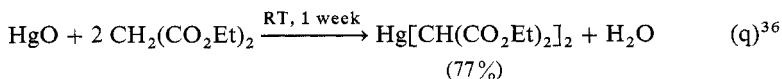


where  $\text{X} = \text{OAc}$  or  $\text{Cl}$ ;  $\text{HgBr}_2$  does not react.

Either  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$  or  $\text{HgO}$  can metallate 1,3-ketones and related compounds<sup>35-39</sup>  $\text{CH}_2(\text{COR})(\text{COR}')$ ;  $\text{R}, \text{R}' = \text{EtO}, \text{EtO}; \text{Me}, \text{Me}; \text{Bu-t}, \text{Bu-t}; \text{EtO}, \text{Me}$ :

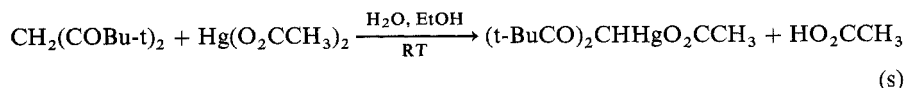


where  $\text{X}_2 = \text{O}$  or  $[\text{N}(\text{SiMe}_3)_2]_2$ ;



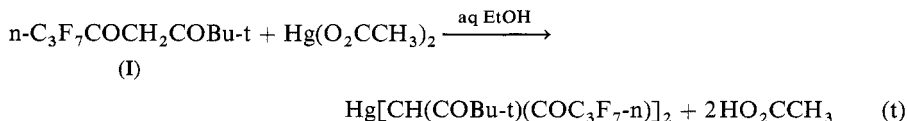
The compound  $\text{CH}_2(\text{CO}_2\text{Et})\text{CN}$  also can be metallated.

Aliphatic 1,3-diketones,  $\text{CH}_2(\text{COR})_2$  ( $\text{R} = \text{Me}^{38}$  or  $\text{Bu-t}^{38,40,41}$ ), e.g., also react with  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in aq  $\text{EtOH}$  to give organomercury salts, e.g.:

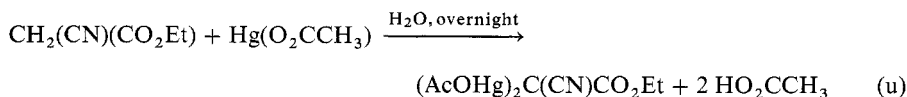


Diorganomercurials,  $\text{Hg}[\text{CH}(\text{COR})_2]_2$ , also can result<sup>42</sup>, especially if xs 1,3-diketone<sup>38</sup> or longer reaction times<sup>40</sup> are used. The diorganomercurial (I), obtained from  $\text{Hg}(\text{OAc})_2$

with  $n\text{-C}_3\text{F}_7\text{COCH}_2\text{COBu-t}$  in aq EtOH, exists in the solid in the  $\text{C-Hg-C}$ -bonded form, but in solution both this and  $\text{C-Hg-O}$  forms are found<sup>42</sup>:



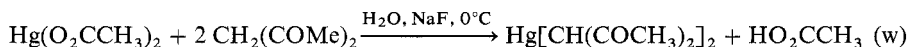
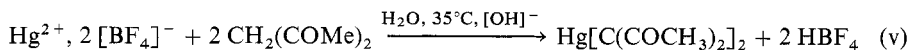
Esters, such as  $\text{CH}_2(\text{CO}_2\text{Et})_2$ ,  $\text{CH}_2(\text{COMe})(\text{CO}_2\text{Et})$  or  $\text{CH}_2(\text{CN})(\text{CO}_2\text{Et})$ , are dimercurated<sup>36</sup> by  $\text{Hg}(\text{OAc})_2$ , e.g.:



as is the diaryl 1,3-diketone<sup>41</sup>,  $(\text{PhCO})_2\text{CH}_2$ .

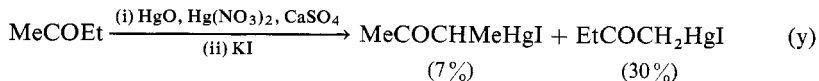
Reactions of aliphatic 1,3-diketones,  $\text{CH}_2(\text{COR})_2$ , with  $\text{HgCl}_2$  at RT provide organomercury chlorides<sup>38,44</sup>,  $\text{ClHgCH}(\text{COR})_2$ , or dimetallated products,  $(\text{ClHg})_2\text{C}(\text{COR})_2$ , depending on the conditions and mol ratios;  $\text{NaOAc}$  also is added to aid formation of the organomercurials<sup>38</sup>. Mercury(II) bromide reacts similarly<sup>36</sup> to  $\text{HgCl}_2$ ;  $\text{Hg}(\text{CN})_2$  and  $\text{HgI}_2$  are inert<sup>34</sup>. Mercury(II) chloride also can dimetallate<sup>36</sup>  $\text{CH}_2(\text{CN})(\text{CO}_2\text{Et})$ .

Changing the reaction conditions can change the mercuriation product; e.g., with  $\text{CH}_2(\text{COMe})_2$  anion-free compounds having Hg:diketone stoichiometres of 1:1, 1:2 and 2:3 are obtained<sup>45</sup>:

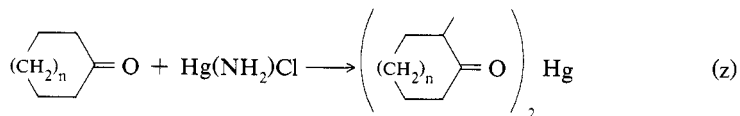


Organomercury bases, e.g.,  $\text{MeHgN}(\text{SiMe}_3)_2$ , also react with 1,3-dicarbonyl compounds<sup>46</sup>.

As shown in Eq. (j), monoketones can react with  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$ ; e.g., cyclohexanone reacts<sup>34</sup> with  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$ . Acetone and related ketones, such as  $\text{MeCOEt}$ ,  $\text{MeCOPr-i}$  and  $\text{MeCOPh}$  are mercurated<sup>18</sup> by  $\text{HgO}$ ,  $\text{Hg}(\text{NO}_3)_2$  and  $\text{CaSO}_4$ , e.g.:

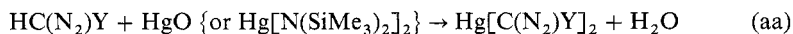


Cycloheptanone and cyclo-octanone can react<sup>19</sup> with  $\text{Hg}(\text{NH}_2)\text{Cl}$  in 30% aq  $\text{HO}_2\text{CCH}_3$ :



where  $n = 2$  or  $3$ . Esters form enolates on reaction<sup>18</sup> with  $\text{HgO}$ ,  $\text{Hg}(\text{NO}_3)_2$  and  $\text{CaSO}_4$ .

Mercuration of diazoalkanes,  $\text{HC}(\text{N}_2)\text{Y}$ , occurs where Y is an electron-withdrawing group such as  $\text{COR}$ <sup>47,48</sup>,  $\text{CO}_2\text{R}$ <sup>2,26,49</sup>,  $\text{CF}_3$ <sup>26</sup>,  $\text{CN}$ <sup>26</sup>,  $\text{NO}_2$ <sup>27</sup>,  $\text{P}(\text{O})\text{R}_2$ <sup>28</sup> or  $\text{P}(\text{O})(\text{OR})_2$ <sup>28,50</sup>. Both  $\text{HgO}$  and  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$  are effective:

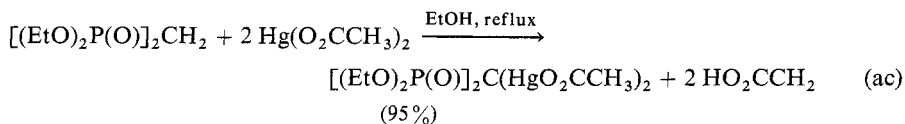


Organomercury bases also react with diazocarbonyl compounds, e.g.<sup>49,51</sup>:



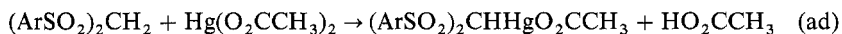
where  $\text{Y} = \text{N}(\text{SiMe}_3)_2$ <sup>49</sup>, or  $\text{OH}$  or  $\text{OEt}$ <sup>51</sup>, and  $\text{R} = \text{Me}$ ,  $\text{Et}$ , etc.;  $\text{R}' = \text{OMe}$ ,  $\text{OEt}$ ,  $\text{OPr-i}$ ,  $\text{OBu-t}$ ,  $\text{OCH}_2\text{Ph}$ , etc.

Phosphonate esters,  $[(\text{EtO})_2\text{P}(\text{O})]\text{RCH}_2$ ,  $\text{R} = (\text{EtO})_2\text{P}(\text{O})$ ,  $\text{EtO}_2\text{C}$  or  $\text{CN}$ , are dimetallated<sup>31</sup> by  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ :

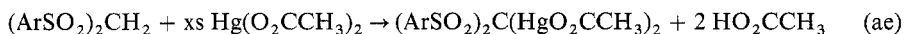


Monomercurated compounds are mercurated more readily than the starting compounds, and hence it is not possible to obtain the monomercurated compounds by limiting the amount of  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ .

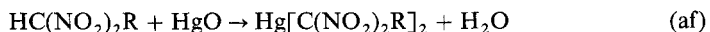
1,3-Disulfonates, however, can be monomercurated:



Dimercurated products are obtained<sup>30</sup> using xs  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ :



Nitromethanes,  $\text{HC}(\text{NO}_2)_2\text{R}$  ( $\text{R} = \text{F}$ <sup>23</sup> or  $\text{NO}_2$ <sup>22</sup>), are monomercurated using  $\text{HgO}$ :

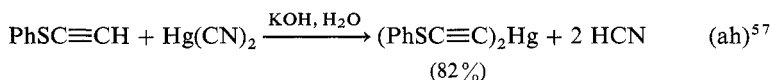


Mercuration<sup>5,24</sup> of polyhaloalkanes  $\text{HCXYR}'$  ( $\text{X}$ ,  $\text{Y} = \text{halides}$ ,  $\text{R}' = \text{halide}$ ,  $\text{CF}_3$ <sup>52</sup>,  $\text{CO}_2\text{R}$ <sup>53</sup>,  $\text{CONR}_2$ <sup>54,55</sup>,  $\text{SO}_2\text{Ph}$ <sup>55</sup> or  $\text{H}$ <sup>56</sup>) can occur:

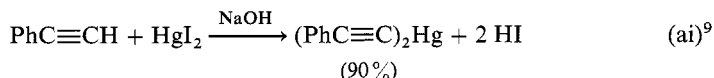


where  $\text{Y} = \text{halide}$ . The base can be  $\text{t-BuOK}$  or  $\text{MeONa}$ ;  $\text{RHgOR}'$  is used also.

Terminal alkynes,  $\text{RC}\equiv\text{CH}$ , also react with  $\text{Hg(II)}$  salts [e.g., Eq. (k)],  $\text{HgX}_2$  and  $\text{R}'\text{HgX}$ . The  $\text{R}$  groups include aryl, alkyl, functionally substituted alkyl groups, perfluoroalkyl, alkoxy and thioalkoxy groups, etc, e.g.:

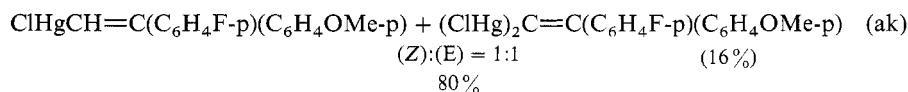
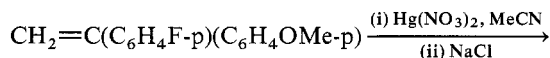
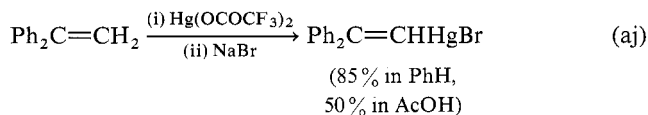


To suppress additions to the triple bond, basic conditions are used, e.g.:

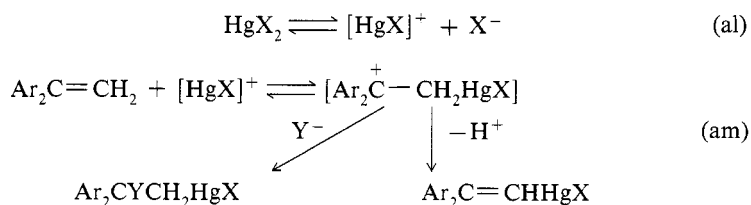


Other mercurating systems for alkynes include  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{MeOH}$ <sup>6</sup>,  $\text{HgO}$  in benzene<sup>7</sup> or  $\text{HgCl}_2$  in the presence of base<sup>7</sup>.

Reaction of  $\text{Hg}$  salts with alkenes leads to addition (solvo- or oxymercuration) to give  $\beta$ -functionally substituted ethylmercurials. However, vinylmercuriation can be obtained; e.g., vinylmercuriation occurs with 1,1-diarylethenes, especially with ionic  $\text{HgX}_2$  containing weakly nucleophilic anions ( $\text{X}^-$ ), such as  $[\text{CF}_3\text{CO}_2]^-$ ,  $[\text{NO}_3]^-$  or  $[\text{BF}_4]^-$  in such solvents as  $\text{MeCN}$ ,  $\text{Et}_2\text{O}$  or  $\text{PhH}$ . Dimercuration products  $\text{Ar}_2\text{C}=\text{C}(\text{HgX})_2$  also may be obtained:

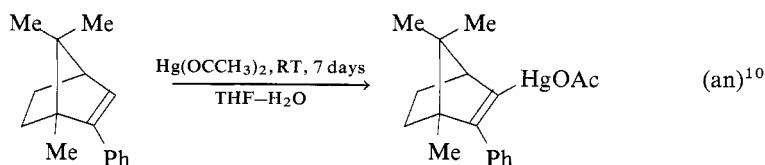


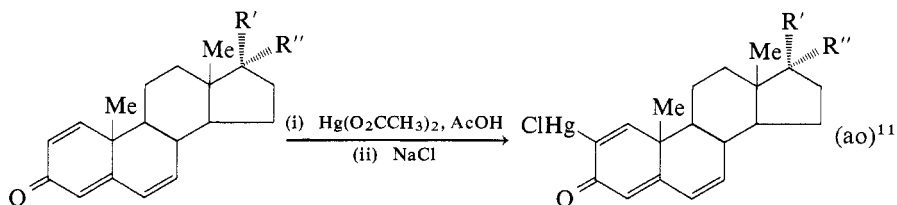
Trisubstituted arylalkenes  $\text{Ar}_2\text{C}=\text{CHY}$ ,  $\text{Y} = \text{Me}$ ,  $\text{Ph}$  or  $\text{Br}$ , do not undergo vinylmercuriation. In the presence of a nucleophile, e.g., as with reactions in  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ , or with reaction in the presence of  $\text{H}_2\text{O}_2$ , or using  $\text{Hg}(\text{OAc})_2$ , solvomercuration will occur, e.g.,  $\text{Hg}(\text{OAc})_2$  with  $\text{Ph}_2\text{C}=\text{CH}_2$  provides solvomercuration products. Both substitution and addition products may occur together<sup>13</sup>, e.g., with  $\text{Hg}(\text{OCOFCF}_3)_2$  and  $\text{Ph}_2\text{C}=\text{CH}_2$  in  $\text{MeOH}$ . The mechanism is:



The complexing ability of the solvent toward the mercuriation species is also important. The greater the complexation with  $\text{HgX}_2$ , the less electrophilic is  $\text{HgX}_2$  and hence less substitution occurs.

Other examples of vinylmercuriation are:





where  $R', R'' = \text{HO, Me; HO, H; AcO, H; O}$ .

In addition,  $\text{Cl}_2\text{C}=\text{CClH}$  also undergoes vinylmercuriation<sup>12</sup> by  $\text{Hg}(\text{CN})_2$ ,  $\text{KOH}$  in  $\text{H}_2\text{O}$  to  $(\text{Cl}_2\text{C}=\text{CCl})_2\text{Hg}$ .

Cyclopentadiene and its derivatives undergo mercuration by  $\text{HgO}$  in the presence of a primary amine<sup>14</sup>, and by<sup>58</sup>  $\text{Hg}[\text{N}(\text{SiMe}_3)_2]_2$ . These reagents provide  $(\text{h}^1\text{-C}_5\text{H}_5)_2\text{Hg}$ . More forcing conditions, e.g., using  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  or  $\text{HgCl}_2$  in the presence of  $\text{NaOAc}$ , provide permercurated cyclopentadienes,  $\text{C}_5(\text{HgX})_6$  ( $\text{X} = \text{Cl}$ , or  $\text{O}_2\text{CCH}_3$ )<sup>16</sup> even at  $25^\circ\text{C}$ .

Mercuration of  $\text{C}_5\text{Cl}_5\text{H}$  at  $0^\circ\text{C}$  by  $\text{Hg}(\text{OMe})_2$  prepared in situ from  $\text{LiOMe}$  and  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  provides<sup>17</sup>  $(\text{C}_5\text{Cl}_5)_2\text{Hg}$ ;  $\text{PhHgOH}$  also reacts with  $\text{C}_5\text{Cl}_5\text{H}$  at  $0^\circ\text{C}$  to give  $\text{PhHgC}_5\text{Cl}_5$ .

Polymermercuration of simple organic compounds, e.g.,  $\text{EtOH}$  by  $\text{HgO}$ , gives polymeric products or mixtures. These are difficult to purify and characterize, with elemental analysis being the only aid. Many proposed structures are erroneous<sup>4</sup>.

(iv) Aromatic Mercuration<sup>4,5,59,60</sup>. Aromatic compounds are metallated by electrophilic Hg salts:



Reactions are achieved with benzene and its derivatives (including those deactivated for electrophilic attack), polycyclic aromatics, heteroaromatics and transition-metal complexes of aromatic ligands.

Polymermercuration frequently occurs. The Hg atom is not large [the non-bonded radius is  $1.50\text{--}1.73 \text{ \AA}$  ( $150\text{--}173 \text{ pm}$ ), compared, e.g., with  $1.95 \text{ \AA}$  ( $195 \text{ pm}$ ) for Br], and its electronic effect is weak. Permercuration of aromatics is possible, and not all compounds require drastic conditions, such as fusion with reactive Hg salts<sup>61,62</sup>. Furan<sup>62</sup>, pyrrole<sup>63</sup>, thiophene<sup>64</sup> and cyclobutadiene iron tricarbonyl<sup>65</sup> are mercurated under mild circumstances. For the monomermercuration of the more reactive aromatics, the extent of reaction must be limited, e.g., by using the mild  $\text{HgCl}_2$  in the presence of  $\text{NaO}_2\text{CCH}_3$  to buffer the solution.

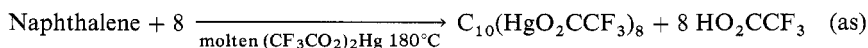
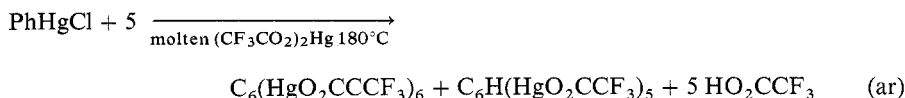
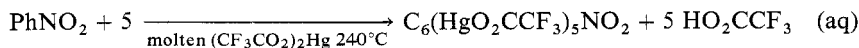
Both heterogeneous, i.e., two-phase aq-hydrocarbon systems, once frequently used<sup>66</sup>, and homogeneous reaction media are used. Use of  $\text{HO}_2\text{OCCH}_3$  as solvent with  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  as the mercurating agent is popular<sup>67,68</sup>; the addition of  $\text{HClO}_4$  (or another strong acid, e.g.,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ) to  $\text{Hg}(\text{O}_2)_2$  in  $\text{HOAc}$  results in a more effective mercuration medium. Use of  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{HO}_2\text{CCH}_3$  is superseded by the more efficient  $\text{Hg}(\text{OCOCF}_3)_2$  in  $\text{CF}_3\text{CO}_2\text{H}$  solution<sup>69–71</sup>.

The enhanced reactivity of  $\text{Hg}(\text{OCOCF}_3)_2$  in  $\text{CF}_3\text{CO}_2\text{H}$  over  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{CH}_3\text{CO}_2\text{H}$  is obvious<sup>70</sup> from the reactivities toward benzene of  $6.9 \times 10^5:1$ . Addition of  $\text{CF}_3\text{SO}_3\text{H}$  to the  $\text{Hg}(\text{OCOCF}_3)_2\text{--CF}_3\text{CO}_2\text{H}$  medium results in a further increase in reactivity<sup>72</sup>.

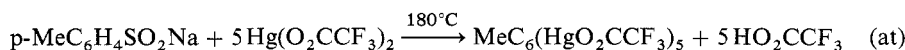


More limited use is made<sup>73</sup> of  $(\text{Cl}_3\text{CCO}_2)_2\text{Hg}$  in  $\text{Cl}_3\text{CCO}_2\text{H}$ . There is no advantage in using the trichloroacetic acid system compared to trifluoroacetic acid.

Reactions also can be carried out without solvent or using molten Hg salts, e.g.,  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  or  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ . The acetate can survive to ca.  $180^\circ\text{C}$ ;  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$  is stable to  $300^\circ\text{C}$ , and is used as a melt without problem to  $240^\circ\text{C}$ . Poly- and even permercuration can occur under these drastic conditions<sup>61,62,74</sup>, e.g.:

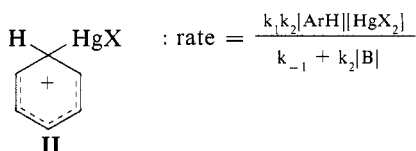
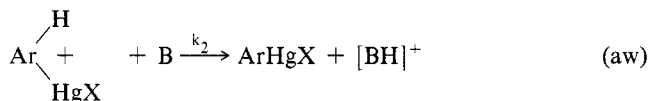
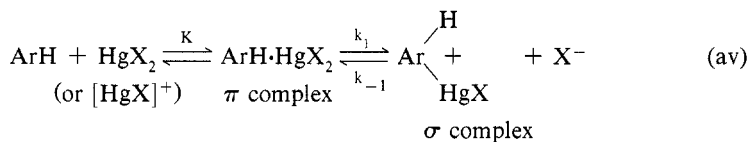


Many groups are secure against replacement, e.g.,  $\text{NO}_2$ , Br, Cl, F, MeO, Me,  $\text{CO}_2\text{Me}$  and  $\text{CF}_3$ . The carboxylate group also may survive, but the  $\text{NaO}_2\text{S}$  group is replaced, e.g.:



The kinetics and mechanisms of these aromatic mercurations are known, e.g., for  $\text{Hg}(\text{OCOCF}_3)_2$ <sup>69,70</sup> and  $\text{Hg}(\text{OAc})_2$ <sup>67</sup>. The most straightforward for kinetic purposes is the  $\text{Hg}(\text{OCOCF}_3)_2$ - $\text{CF}_3\text{CO}_2\text{H}$  system. Clean second-order reactions (first order in Hg salt and in aromatic) are found at all concentrations. For the  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ - $\text{CH}_3\text{CO}_2\text{H}$  system (with or without  $\text{HClO}_4$ ), there is departure from second-order kinetics at other than low concentrations. Another problem with reaction in AcOH is solvent mercuration.

The mechanism involves rapid formation of a  $\pi$  complex with subsequent slower reactions to  $\sigma$  complexes [e.g., (II) for PhH], and hence to products:

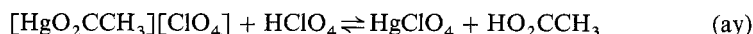


However, variations are expected among the systems used for mercuration.

Pi complexes are indicated by the increase in absorption in the region 280–310 nm on mixing ArH and  $\text{Hg}(\text{OCOCF}_3)_2$  in  $\text{CF}_3\text{CO}_2\text{H}$  solution; values of  $K$  ( $\text{L mol}^{-1}$ ) are calculated to be 0.8, 1.0, 8.2, 10 and 40 for  $\text{ArH} = \text{PhCl}, \text{PhF}, \text{PhH}, \text{PhMe}$  and  $o\text{-MeC}_6\text{H}_4$ , respectively<sup>69</sup>.

Sigma complexes, or mercurinium ions, are detected<sup>75,76</sup> by NMR from certain arene-mercury salt interactions; e.g., from the interaction<sup>77</sup> of pentamethylbenzene with  $\text{Hg}(\text{OCOCF}_3)_2$  in  $\text{CF}_3\text{CO}_2\text{H}$ . Others are detected in weakly nucleophilic media, such as liq  $\text{SO}_2$ . A primary hydrogen isotope effect is experienced in Eq. (av) (rate constant  $k_2$ ). The importance of  $k_2$  and  $k_{-1}$  in the kinetic expression can be seen in the values of hydrogen isotope effects. For example, a  $k_{\text{H}}/k_{\text{D}}$  value of  $6.0 \pm 0.1$  is found<sup>78</sup> for mercuriation of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  by  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  (0.051 M) in  $\text{HO}_2\text{CCH}_3$  containing  $\text{H}_2\text{O}$  (0.23 M) and  $\text{HClO}_4$  catalyst (0.32 M) at  $25^\circ\text{C}$  and values<sup>79</sup> of 3.6 and 7.2 for the uncatalyzed and  $\text{HClO}_4$ -catalyzed mercuriation of naphthalene by  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{CH}_3\text{CO}_2\text{H}$ . The  $k_{\text{H}}/k_{\text{D}}$  values determined in  $\text{CF}_3\text{CO}_2\text{H}$  solution are dissected into components for  $\pi$ -complex formation and for the subsequent steps to products. For example, the  $k_{\text{H}}/k_{\text{D}}$  value of 5.6 for PhH is composed of values of 1.5 for formation of the  $\text{PhH-Hg}(\text{OCOCF}_3)_2$   $\pi$  complex and 3.7 for reaction to products<sup>69</sup>.

The catalytic effects of the  $\text{HClO}_4$  (or other strong acids containing weakly nucleophilic anions, e.g.,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ ) in  $\text{HO}_2\text{CCH}_3$  and of  $\text{CF}_3\text{SO}_3\text{H}$  in  $\text{CF}_3\text{CO}_2\text{H}$  reaction arise from anion exchanges, which lead to more reactive mercurating agents, e.g.:



Anions strongly catalyze mercurations in  $\text{H}_2\text{O}$  as a consequence of replacing aquo ligands from the coordination sphere of the  $\text{Hg}^{2+}$ .

In uncatalyzed mercurations by  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{HO}_2\text{CCH}_3$ , the more significant electrophilic entity in the absence of added catalysts is unionized  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ , although  $[\text{HgO}_2\text{CCH}_3]^+$  also plays a role, as found<sup>80</sup> with PhOMe.

In keeping with its electrophilic nature, the presence of electron-withdrawing groups hinders, and electron-donating agents foster, the reaction (see Table 2). Therefore, more vigorous conditions are required for arenes bearing more electron-withdrawing groups. The rates correlate with  $\sigma^+$  values<sup>60</sup>, with negative values of the  $\rho$  factors, e.g.,  $-4.0$  for the uncatalyzed reactions of  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{HO}_2\text{CCH}_3$ ,  $-5.1$  for the  $\text{HClO}_4$ -catalyzed reactions of  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$  in  $\text{HO}_2\text{CCH}_3$ , and  $-5.7$  for the  $\text{Hg}(\text{OCOCF}_3)_2\text{-CF}_3\text{CO}_2\text{H}$  reaction.

As a preparative route mercuriation of arenes suffers from a lack of selectivity; often all possible ring substitution products are formed. The directing influences of substituents operate, but selectivity is poor. The initial products can isomerize. Isomer distributions in mercuriation of toluene under different conditions are given in Table 3. These effects coupled with the ease of polymercuration can be disadvantageous. Mild conditions must be used to limit the extent of mercuriation of five-membered heterocyclic aromatics such as pyrrole, thiophene, selenophen and furan. These are among the most reactive aromatics toward Hg salts; use of  $\text{HgCl}_2$  in the presence of  $\text{NaO}_2\text{CCH}_3$  at RT is

TABLE 2. RATE CONSTANTS FOR MERCURATION OF AROMATICS

Compound	Rate constants			
	Hg(OAc) <sub>2</sub> , HOAc (50°C)	Hg(OAc) <sub>2</sub> , HClO <sub>4</sub> AcOH (25°C)	Hg(OCOCF <sub>3</sub> ) <sub>2</sub> CF <sub>3</sub> CO <sub>2</sub> H (25°C)	
	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> ) <sup>a,b,c</sup>	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> ) <sup>b,c,d</sup>	10 <sup>2</sup> k <sub>obs</sub> (s <sup>-1</sup> ) <sup>b,e,f</sup>	10 <sup>2</sup> k <sub>obs</sub> (s <sup>-1</sup> ) <sup>b,d,g,69</sup>
PhH	0.075	43	2.85	2.92
PhMe	0.382	387	28.2	51.0
PhEt	0.325	330	24.4	—
PhPr-i	0.303	303	21.1	—
PhBu-t	0.248	271	17.2	—
1,2-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1.26	1,370	—	281
1,3-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2.70	38,400	—	—
1,4-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0.640	538	—	—
1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	16.5	—	—	—
1,2,4,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	2.37	—	—	—
PhF	—	16.0	0.818	0.61
PhCl	—	2.27	0.134	0.083
PhBr	—	2.00	0.113	—
PhI	—	1.82	—	—
PhNO <sub>2</sub>	—	0.0177	—	—
PhPh	—	179	—	—
Naphthalene	—	523	—	—
PhHgOAc	—	29.5	—	—

<sup>a</sup> From ref. 60.

<sup>b</sup> p ≈ -4.0.

<sup>c</sup> From ref. 59.

<sup>d</sup> d[ArH]/dt = k<sub>obs</sub>[ArH] (under pseudo-first-order conditions).

<sup>e</sup> p ≈ -5.1.

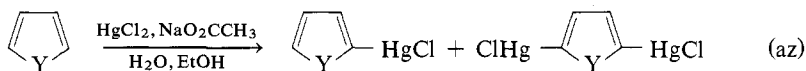
<sup>f</sup> p ≈ -5.7.

<sup>f</sup> p ≈ -6.4.

<sup>f</sup> From ref. 70.

<sup>g</sup> From ref. 69.

recommended over use of the more reactive Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>. Preferred reaction is at position 2 or 5, e.g.:



where Y = O<sup>83</sup> or S<sup>84</sup>.

In contrast, the six-membered heteroaromatic, pyridine, is deactivated toward electrophiles and for pyridine, use of Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> at 155°C is necessary. The product is 3-pyridylmercury acetate<sup>85</sup>.

Further examples are listed in Table 4.

For phenols and primary or secondary aromatic amines, initial reaction can occur at the OH or NH groups to give O—Hg or N—Hg-bonded species. Subsequent reaction leads to ring substitution, especially at lower pH. Phenols<sup>82,83</sup> and aromatic amines<sup>84-86</sup>

TABLE 3. ISOMER DISTRIBUTION IN MERCURATION OF TOLUENE

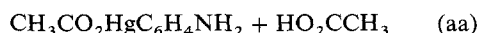
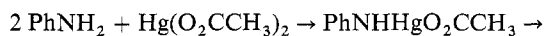
Mercuration conditions	Isomer distribution (%)			Reaction time	Ref.
	o	m	p		
Hg(OAc) <sub>2</sub> in refluxing toluene	41	21	37 <sup>a</sup>		81
Hg(OAc) <sub>2</sub> in toluene at 90°C	32	16	52 <sup>b</sup>		67,68
Hg(ClO <sub>4</sub> ) <sub>2</sub> , 40% HClO <sub>4</sub> at 25°C	19	7	74 <sup>a</sup>		82
Hg(ClO <sub>4</sub> ) <sub>2</sub> , 20% HClO <sub>4</sub> at 85°C	27	13	60 <sup>a</sup>		82
Hg(OCOCF <sub>3</sub> ) <sub>2</sub> in CF <sub>3</sub> CO <sub>2</sub> H at 18°C	28	9	63 <sup>c</sup>	(i) 0	102
	40	13	47	(ii) 3 h	
	45.5	14.5	39.5	(iii) 6 h	
	38	33	29	(iv) 26.25 h	
	31	38	31	(v) 3 days	

<sup>a</sup> Ratio determined by converting MeC<sub>6</sub>H<sub>4</sub>Hg <sup>82</sup>Br into MeC<sub>6</sub>H<sub>4</sub> <sup>82</sup>Br.

<sup>b</sup> Analysis by IR.

<sup>c</sup> Analysis by <sup>1</sup>H NMR.

are reactive, and for these compounds reaction with Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> in H<sub>2</sub>O at RT provides mono- and even dimercuration products:



Use of xs aromatic limits the extent of dimercuration of aromatic amines<sup>84</sup>.

Prior complexation of the Hg salt by the azo group of azobenzenes results in ortho-substitution<sup>87-89</sup>:

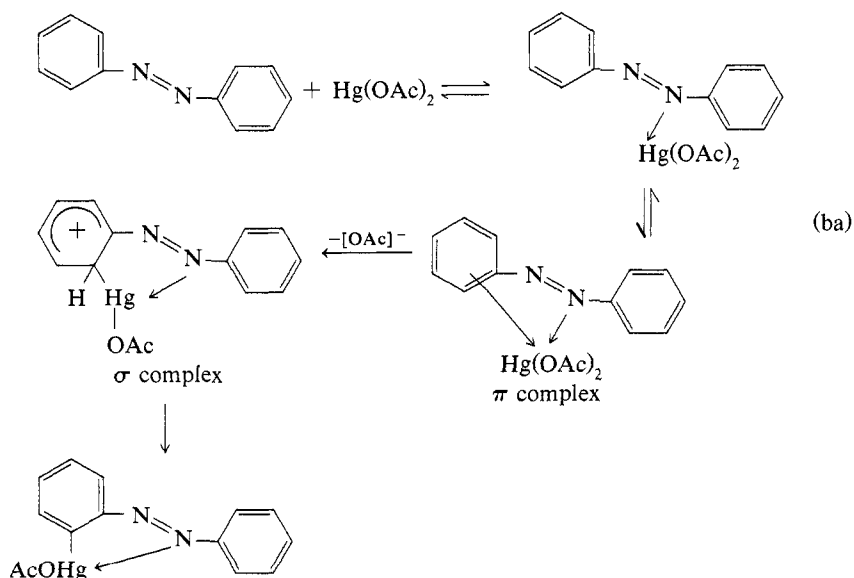


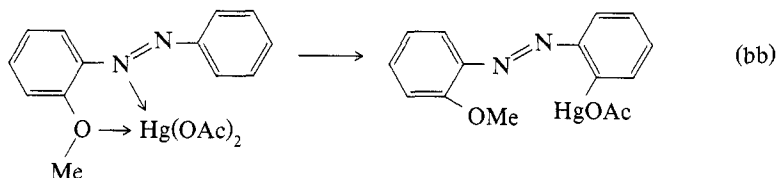


TABLE 4. MERCURATION OF AROMATIC COMPOUNDS

Compound	Reagents and conditions	Product (yield, %)	Ref.
PhOH	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, RT	o- and p-HOC <sub>6</sub> H <sub>4</sub> HgOAc + disubstituted product	86
2,6-t-Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OH	Hg(OAc) <sub>2</sub> , 75% HOAc, 20°C	2,6-t-Bu <sub>2</sub> -4-AcOHgC <sub>6</sub> H <sub>2</sub> OH	90
p-RC <sub>6</sub> H <sub>4</sub> OH	(i) Hg(OAc) <sub>2</sub> , H <sub>2</sub> O (ii) Cl <sup>-</sup>	4-R-2-ClHgC <sub>6</sub> H <sub>3</sub> OH	88
PhOMe	Hg(OAc) <sub>2</sub> (deficit)	p- and o-MeOC <sub>6</sub> H <sub>4</sub> HgOAc	89
PhNH <sub>2</sub>	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, AcOH, NaHCO <sub>3</sub>	2,4-(AcOHg) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub> (93)	92
o-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O [ArNH <sub>2</sub> : Hg = 4 : 1]	4-AcOHg-2-MeC <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	90
m-Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Hg(OAc) <sub>2</sub> , AcOH, HClO <sub>4</sub> , RT	2,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> HgOAc	91
PhH	Hg(OCOCF <sub>3</sub> ) <sub>2</sub> , CF <sub>3</sub> CO <sub>2</sub> H, 25°C	PhHgOCOCF <sub>3</sub>	70
p-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Hg(OAc) <sub>2</sub> , AcOH, reflux	2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> HgOAc (50)	93
PhCF <sub>3</sub>	(i) HgO, HClO <sub>4</sub> , H <sub>2</sub> O (ii) NaCl	m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> HgCl + 3,5-(ClHg) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CF <sub>3</sub>	94
PhNHCOMe	Hg(OAc) <sub>2</sub> , Δ, H <sub>2</sub> O	p-AcOHgC <sub>6</sub> H <sub>4</sub> NHCOMe	95
PhNO <sub>2</sub>	(i) HgO, liq HF, 10 h (ii) KBr (i) Hg(OAc) <sub>2</sub> , 150°C (ii) NaCl	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> HgBr (91%) o-, m- or p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> HgCl [53 : 32 : 15]	96 97
	(i) HgO, 60% HClO <sub>4</sub> , 10 days, RT (ii) NaCl	(o- + p-) : m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> HgCl [11 : 89]	98
	(i) Hg(OAc) <sub>2</sub> , PhNO <sub>2</sub> , 95°C (ii) NaCl	(o- + p-) : m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> HgCl [52 : 48]	98
1,2,3-Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	Hg(O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> , Δ	(2,3,4-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> Hg	99
p-NO <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> H	Hg(O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> , 220°C	(p-NO <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> ) <sub>2</sub> Hg	93
p-MeOC <sub>6</sub> F <sub>4</sub> H	(i) Hg(OCOCF <sub>3</sub> ) <sub>2</sub> , CF <sub>3</sub> SO <sub>3</sub> H, CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 10 min (ii) HCl	p-MeOC <sub>6</sub> F <sub>4</sub> HgCl (72)	71
p-BrC <sub>6</sub> F <sub>4</sub> H	(i) Hg(OCOCF <sub>3</sub> ) <sub>2</sub> , CF <sub>3</sub> SO <sub>3</sub> H, CF <sub>3</sub> CO <sub>2</sub> H, 73°C, 18 h (ii) HCl	p-BrC <sub>6</sub> F <sub>4</sub> HgCl (80)	71
C <sub>6</sub> F <sub>5</sub> H	Hg(O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> , 150°C	C <sub>6</sub> F <sub>5</sub> HgO <sub>2</sub> CCF <sub>3</sub> (85)	95
C <sub>6</sub> Cl <sub>5</sub> H	Hg(OCOCF <sub>3</sub> ) <sub>2</sub> , Δ	(C <sub>6</sub> Cl <sub>5</sub> ) <sub>2</sub> Hg	99
	HgCl <sub>2</sub> , NaOAc, H <sub>2</sub> O, EtOH	 HgCl	100
Naphthalene	Hg(OAc) <sub>2</sub> , AcOH	2-C <sub>10</sub> H <sub>7</sub> HgOAc (95%) + 2-C <sub>10</sub> H <sub>7</sub> HgOAc	77

The rigid *cis*-azo compound, benzo[*c*]cinnoline, does not give mercuration products under the same conditions owing to the impossibility of achieving the *trans* geometry required for the assisted mercuration<sup>89</sup>.

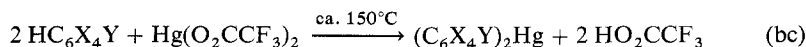
Mercuration of 2-MeOC<sub>6</sub>H<sub>4</sub>N=NPh occurs in the phenyl ring to give 2-MeOC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>HgX, despite the substantial electron-donating effect of the MeO group, which renders the 2-MeOC<sub>6</sub>H<sub>4</sub> ring more electron rich. The MeO group is also coordinated to the Hg electrophile, and this is ideal for the Hg to enter the unsubstituted ring in an assisted reaction:



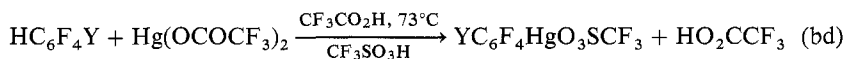
Ortho-mercuration also occurs<sup>90</sup> with ArCH=NNHC<sub>6</sub>H<sub>4</sub>Y. Benzene itself is mercured<sup>4</sup>, including by Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> in glacial HO<sub>2</sub>CCH<sub>3</sub> at 100°C over 5 h (or in an autoclave)<sup>4</sup>; by reaction with a mixture<sup>91</sup> of Hg(NO<sub>3</sub>)<sub>2</sub>, HgO and CaSO<sub>4</sub><sup>91</sup>; by<sup>92</sup> Hg[C(NO<sub>2</sub>)<sub>3</sub>]<sub>2</sub> and most readily by Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> in CF<sub>3</sub>CO<sub>2</sub>H at RT<sup>67,68</sup>.

Halobenzenes are metallated<sup>4</sup> by heating with Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> at >90°C<sup>4</sup>.

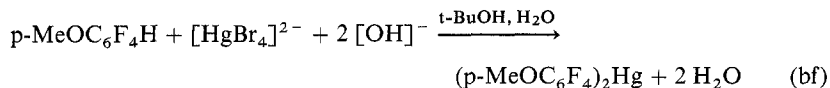
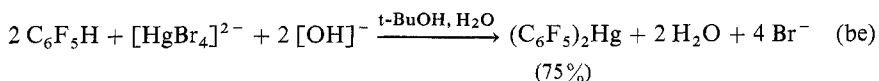
For arenes that are deactivated toward electrophiles, e.g., polychloro-<sup>93</sup> and polyfluorobenzenes<sup>94</sup>, heating with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> to ca. 150°C works, e.g.:



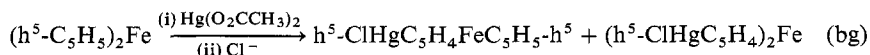
as does reaction with the most powerful combination<sup>71</sup> Hg(OCOCF<sub>3</sub>)<sub>2</sub>-CF<sub>3</sub>SO<sub>3</sub>H-CF<sub>3</sub>CO<sub>2</sub>H:



where X = F, *p*-HO, *p*-MeO, *p*-NH<sub>2</sub>, *o*-H, *p*-H, *m*-Br, *p*-Br, *m*-CO<sub>2</sub>H, *p*-NO<sub>2</sub>. Mono- or dimercuration of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, depending on conditions, occurs on heating at 150°C with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>; with Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> only monomercuration results. Polyhalo substitution renders such arenes acidic and liable to mercuration by reaction with Hg salts under basic conditions. This method can be too severe for certain groups<sup>94-96</sup>:

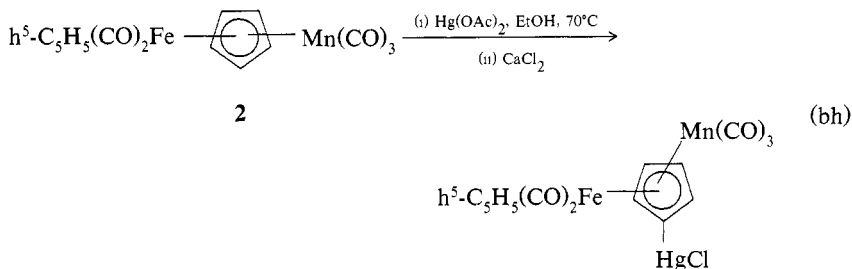


Transition-metal complexes containing cyclopentadiene and cyclobutadiene ligands are mercured readily, e.g., ferrocene<sup>97,98</sup>, (h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe, reacts with Hg(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> in HO<sub>2</sub>CCH<sub>3</sub>, Et<sub>2</sub>O-EtOH, or PhH-EtOH to give mixtures of mono- and dimercurated ferrocenes in proportions dependent on the reagents' ratio<sup>94</sup>:

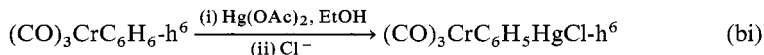


Permercuration of ferrocene is achieved<sup>99</sup> using  $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ . Substituted ferrocenes also can be mercured; e.g., with  $\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{X}$  (i) if X is an electron-withdrawing group, e.g.,  $\text{RCO}$  or  $\text{RO}_2\text{C}$ , mercuration occurs at the 2 and 1' sites<sup>100</sup>; (ii) if X is a halogen<sup>101</sup>, or  $\text{t-Bu}$ <sup>102</sup>, substitution is in the 3- and 1'-positions and (iii) if X is  $\text{PhN=N}$ , substitution occurs at the 2-position<sup>103</sup>.

Other  $\pi$ -bonded cyclopentadiene complexes to be mercured include  $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Ru}$ <sup>104</sup>,  $\text{h}^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3$  ( $\text{M} = \text{Mn}$ <sup>105</sup> or  $\text{Re}$ <sup>106</sup>),  $\text{h}^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{PPh}_3$  ( $\text{M} = \text{Mn}$  or  $\text{Re}$ )<sup>107</sup>,  $\text{h}^5\text{-MeC}_5\text{H}_4\text{Mn}(\text{CO})_3$ <sup>105</sup>,  $\text{h}^5\text{-C}_5\text{H}_5\text{CoC}_4\text{Ph}_4\text{-h}^4$ <sup>108</sup> and compound (2)<sup>109</sup>:



Cyclobutadiene iron tricarbonyl is permercured easily<sup>63</sup>, but benzenechromium tricarbonyl is less reactive than free benzene<sup>110</sup>:



(J. L. WARDELL)

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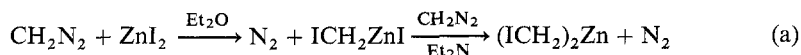


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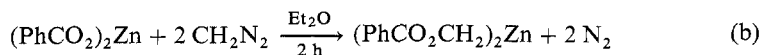
121. O. A. Reutov, V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov, I. A. Amiraslanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2147 (1977).  
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### 5.7.2.3.5. with Diazoalkanes.

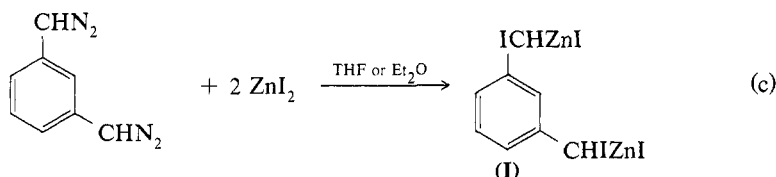
(i) Zinc. Diazomethane with  $\text{ZnI}_2$  in  $\text{Et}_2\text{O}$  gives<sup>1</sup>  $\text{ICH}_2\text{ZnI}$  and, with xs  $\text{CH}_2\text{N}_2$ ,  $(\text{ICH}_2)_2\text{Zn}$ ; i.e., methylene insertion into the Zn-halide bond occurs:



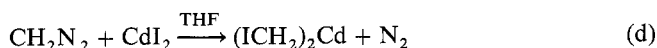
Bis(chloromethyl)zinc can be prepared similarly from  $\text{CH}_2\text{N}_2$  and  $\text{ZnCl}_2$  in<sup>1</sup>  $\text{Et}_2\text{O}$  or<sup>2</sup> dioxane; however,  $(\text{ClCH}_2)_2\text{Zn}$  decomposes in  $\text{Et}_2\text{O}$  to give  $\text{ZnO}$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$  and  $\text{C}_4\text{H}_{10}$ . Methylene insertion into the Zn—O bonds of Zn benzoate also occurs<sup>3</sup> on reaction with diazomethane to give  $(\text{PhCO}_2\text{CH}_2)_2\text{Zn}$ :



The bis-diazoalkane compound, 1,3-bis(diazomethyl)benzene, reacts with  $\text{ZnI}_2$  in tetrahydrofuran (THF) or  $\text{Et}_2\text{O}$  to give the bis(organozinc) compound (I). The carbenoid (I) is more stable<sup>4</sup> in THF than in  $\text{Et}_2\text{O}$ :

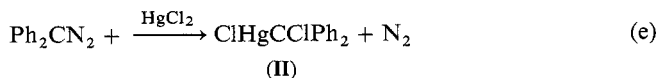


(ii) Cadmium. Bis(iodomethyl)cadmium is obtained<sup>1</sup> from the reaction of  $\text{CH}_2\text{N}_2$  and  $\text{CdI}_2$  in THF:



(iii) Mercury. Mercury halides,  $\text{HgX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ), also react with  $\text{CH}_2\text{N}_2$  to give  $\text{XCH}_2\text{HgX}$  or  $(\text{XCH}_2)_2\text{Hg}$  depending on the mole ratios. Diethylether is the usual solvent; however, a higher yield of  $(\text{ICH}_2)_2\text{Hg}$  (75%) is obtained in dioxane<sup>1</sup>.

Other diazoalkanes also are used. Both diphenyldiazomethane<sup>5</sup> and trifluorodiazomethane<sup>6</sup> react like  $\text{CH}_2\text{N}_2$  does:

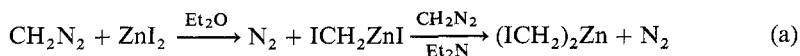


318 5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.2. Carbon-Group-IIB Bonds  
 5.7.2.3. from Metal Salts

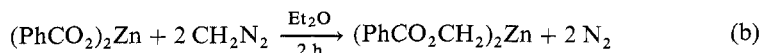
121. O. A. Reutov, V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov, I. A. Amiraslanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2147 (1977).  
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5.7.2.3.5. with Diazoalkanes.

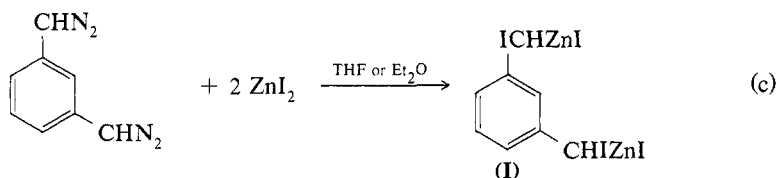
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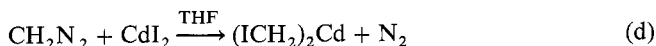
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The bis-diazoalkane compound, 1,3-bis(diazomethyl)benzene, reacts with  $\text{ZnI}_2$  in tetrahydrofuran (THF) or  $\text{Et}_2\text{O}$  to give the bis(organozinc) compound (I). The carbenoid (I) is more stable<sup>4</sup> in THF than in  $\text{Et}_2\text{O}$ :

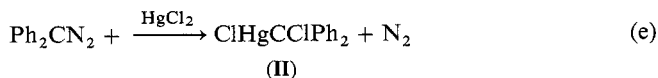


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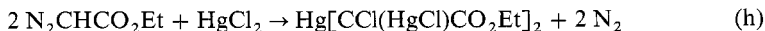
Other diazoalkanes also are used. Both diphenyldiazomethane<sup>5</sup> and trifluorodiazomethane<sup>6</sup> react like  $\text{CH}_2\text{N}_2$  does:



At  $\text{Ph}_2\text{CN}_2:\text{HgCl}_2$  ratios greater than 1:1 in THF, additional insertion of  $\text{CPh}_2$  can occur<sup>7</sup>:

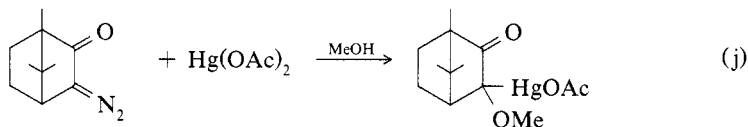
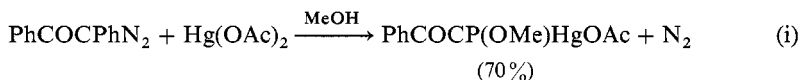


Other substituted diazoalkanes react differently. On reaction with  $\text{HgCl}_2$ , such diazoesters as  $\text{N}_2\text{CHCO}_2\text{Et}$  provide products that result from both insertion and mercuration of the acidic  $\alpha$  hydrogen<sup>8</sup>:

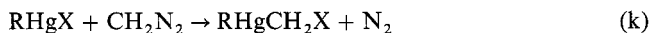


Metallation of the acidic hydrogens of diazo compounds (see §5.7.2.3.4) occurs; even diazomethane can be metallated<sup>9</sup>, e.g., by  $\text{Hg}(\text{OAc})_2$  [ $\text{OAc}$  is  $\text{OC}(\text{O})\text{CH}_3$ ], to give polymeric,  $[\text{HgC}(\text{N}_2)]$  and  $\text{Hg}[\text{CH}(\text{N}_2)]_2$ .

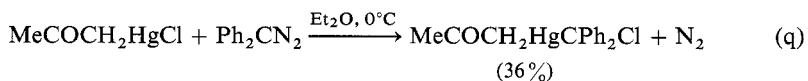
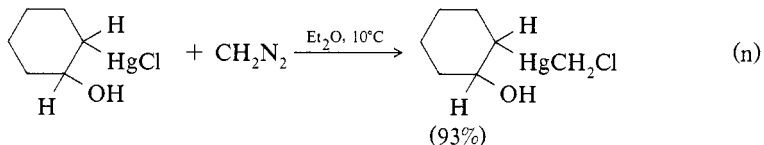
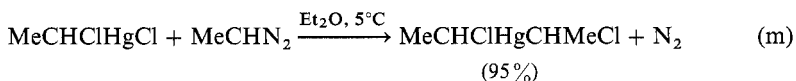
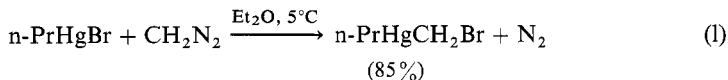
Diazoketones containing no  $\alpha$  hydrogens react differently; e.g., reactions with  $\text{Hg}(\text{OAc})_2$  in the presence of a nucleophile give insertion products incorporating the nucleophile<sup>10</sup>, e.g.:



As well as  $\text{HgX}_2$ , organomercurials  $\text{RHgX}$  also can react with diazoalkanes:



where X = halide or carboxylate. The organic groups, R, taking part in these reactions of organomercury halides include alkyl<sup>11</sup>,  $\alpha$ -haloalkyl<sup>11</sup>,  $\beta$ -hydroxy- and  $\beta$ -alkoxyalkyl<sup>11</sup>,  $\beta$ -oxoalkyl<sup>11</sup>, trichloromethyl<sup>12</sup>, benzyl<sup>5,13</sup>, and aryl<sup>5,11</sup>, e.g.:



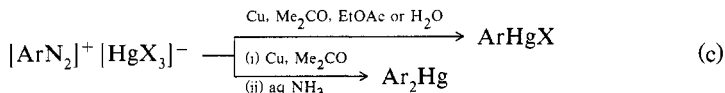
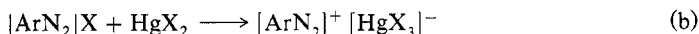
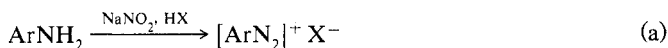
$$2 \text{ p-MeCOC}_6\text{H}_4\text{HgCH}_2\text{Cl} + \frac{\text{Et}_2\text{O}}{\text{CH}_2\text{N}_2} \rightarrow (\text{ClCH}_2)_2\text{Hg} + (\text{p-MeCOC}_6\text{H}_4)_2\text{Hg} \quad (\text{r})$$

(53%)                      (23%)                      (23%)

$$\text{ArHgOCOR} + \text{CH}_2\text{N}_2 \rightarrow \text{ArHgCH}_2\text{OCOR} + \text{N}_2 \quad (\text{s})$$

1. G. Wittig, K. Schwarzenbach, *Justus Liebigs Ann. Chem.*, **650**, 1 (1962).
2. D. Seyferth, *Chem. Rev.*, **55**, 1158 (1955).
3. G. Wittig, M. Jautelet, *Justus Liebigs Ann. Chem.*, **702**, 24 (1967).
4. S. H. Goh, K. C. Chan, H. L. Chong, *Aust. J. Chem.*, **29**, 1699 (1976).
5. L. Hellerman, M. D. Newman, *J. Am. Chem. Soc.*, **54**, 2859 (1932); see also R. Freidlina, A. N. Nesmeyanov, F. A. Tokareva, *Zh. Obshch. Khim.*, **7**, 262 (1937).
6. B. L. Dyatkin, E. P. Mochalina, *Bull. Acad. Sci. USSR (Engl. Transl.)*, 1136 (1964).
7. A. Ledwith and L. Phillips, *J. Chem. Soc.*, 5969 (1965).
8. A. N. Nesmeyanov, G. S. Povkh, *Zh. Obshch. Khim.*, **4**, 958 (1934).
9. A. N. Wright, A. W. Kramer, G. Steel, *Nature (London)* **193**, 903 (1963).
10. A. S. Gudkova, M. Ya. Aleinikova, O. A. Reutov, *Bull. Acad. Sci. USSR (Engl. Transl.)*, 1165 (1966).
11. J. Barluenga, P. J. Campos, J. C. Garcia-Martin, M. A. Roy, G. Asensco, *Synthesis*, 893 (1979).
12. R. Kh. Freidlina, F. K. Velichko, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1225 (1959).
13. R. Scheffold, U. Michel, *Angew. Chem., Int. Ed. Engl.*, **11**, 231 (1972).
14. P. Pfeiffer, R. Schulze-Bentrop, K. H. La Roche, E. Sumitz, *Chem. Ber.*, **85**, 232 (1952).
15. P. Pfeiffer, A. Jager, *Chem. Ber.*, **80**, 1 (1947).

The catalyzed decompositions of the complex (or double) salts of aromatic diazonium halides and Hg(II) halides,  $[\text{ArN}_2]^+[\text{HgX}_3]^-$ , yield organomercurials. Either mono- or diorganomercurials can be produced in these free-radical reactions<sup>1-4</sup>.



The arenediazonium halides are obtained from aromatic amines (on diazotization by one of the standard methods<sup>1,7</sup>, e.g., using  $\text{NaNO}_2$  and aq  $\text{HCl}$  near  $0^\circ\text{C}$ ). The double salts can be obtained as precipitates simply by mixing solutions of the arenediazonium

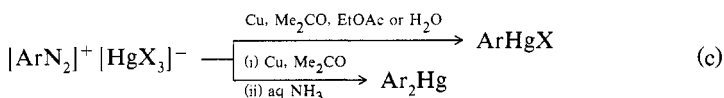
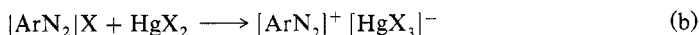
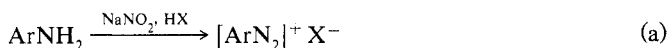
$$2 \text{ p-MeCOC}_6\text{H}_4\text{HgCH}_2\text{Cl} + \frac{\text{Et}_2\text{O}}{\text{CH}_2\text{N}_2} \rightarrow (\text{ClCH}_2)_2\text{Hg} + (\text{p-MeCOC}_6\text{H}_4)_2\text{Hg} \quad (\text{r})$$

(53%)                      (23%)                      (23%)

$$\text{ArHgOCOR} + \text{CH}_2\text{N}_2 \rightarrow \text{ArHgCH}_2\text{OCOR} + \text{N}_2 \quad (\text{s})$$

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The catalyzed decompositions of the complex (or double) salts of aromatic diazonium halides and Hg(II) halides,  $[\text{ArN}_2]^+[\text{HgX}_3]^-$ , yield organomercurials. Either mono- or diorganomercurials can be produced in these free-radical reactions<sup>1-4</sup>:



The arenediazonium halides are obtained from aromatic amines (on diazotization by one of the standard methods<sup>1,7</sup>, e.g., using  $\text{NaNO}_2$  and aq  $\text{HCl}$  near  $0^\circ\text{C}$ ). The double salts can be obtained as precipitates simply by mixing solutions of the arenediazonium

salt and Hg(II) halide in solvents; they can be collected, washed, dried and even stored if suitable precautions are taken.

Decomposition of the double salts to ArHgX is achieved in organic media, e.g., in<sup>2</sup> Me<sub>2</sub>CO or EtOAc, or equally well in<sup>8</sup> H<sub>2</sub>O. The solid double salt is added in small portions to a stirred suspension of Cu powder in the solvent (ca. 30–50 mL of solvent per 10 g double salt) at ca. 0°C for decompositions in H<sub>2</sub>O and –50° to –20°C in Me<sub>2</sub>CO solutions. Complete consumption of the diazonium salt can be tested for using 2-naphthol. In decompositions in H<sub>2</sub>O, the organomercurials separate, whereas in decompositions in organic solvents evaporation of the solvent and extraction of the residue by a solvent is used to obtain ArHgX.

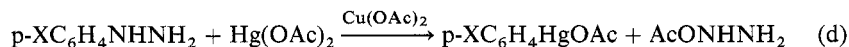
For formation of diorganomercurials, decomposition of the double salt is carried out in acetone (Table 1). Aqueous NH<sub>3</sub> is added subsequently, and the reaction medium is set aside for a period. Addition of H<sub>2</sub>O precipitates the Ar<sub>2</sub>Hg.

As an alternative to using isolated double salts, 1:1 mixtures of ArN<sub>2</sub>X and HgX<sub>2</sub> are used. This approach is valuable for those arenediazonium salts, e.g., RO<sub>2</sub>C- or HO<sub>3</sub>S-substituted arenediazonium compounds, from which it is difficult to isolate pure double salts<sup>11</sup>.

If the aromatic amines are available, then there are some advantages to using the diazonium salt-route to arylmercurials: e.g., (i) Functional groups inert to the diazonium salt reaction conditions include CO<sub>2</sub>H, CO<sub>2</sub>R, SO<sub>3</sub>H and NO<sub>2</sub>—all of which are reactive toward organomagnesium halides or organolithiums. However, vigorous stirring and lower T are required for those reactions involving aromatics bearing electron-withdrawing groups. Such precautions are necessary to limit substitution of the diazonium function by the nucleophiles present, e.g., halides<sup>12</sup>, and (ii) the replacement of the NH<sub>2</sub> function by HgX in ArNH<sub>2</sub> is regiospecific. Hence, only one isomer of ArHgX (or Ar<sub>2</sub>Hg) is obtained, in contrast, e.g., to mercuration of ArH.

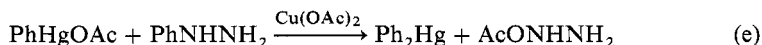
As well as benzenoid compounds, polynuclear aromatic<sup>8,11</sup> and heteroaromatic amines<sup>14,15</sup> are converted to arylmercurials.

Alternatives to ArNH<sub>2</sub> as sources of arenediazonium salts are arylhydrazines<sup>16</sup>:

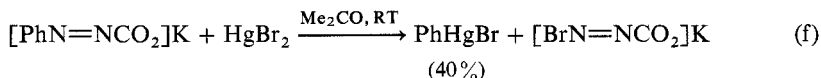


where X = H, Br or NO<sub>2</sub>.

Organomercury salts also react<sup>16</sup>:



Reactions of potassium arylazocarboxylates with Hg halides also lead to arylmercury salts in good yield:



Arylmercury halides also can react with the arylazo carboxylates<sup>17</sup>.

(J. L. WARDELL)

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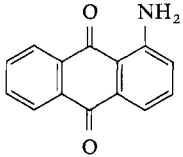
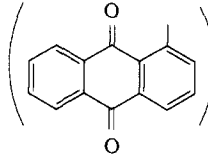
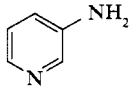
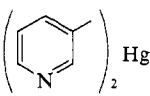
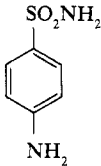
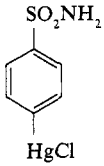
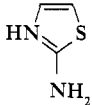
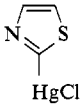
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Table 1. Formation of Arylmercurials from Aromatic Amines via Diazonium Salts

Amine	Conditions <sup>a</sup>	Product (Yield, %) <sup>b</sup>	Ref.
PhNH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, -10°C	PhHgCl (60)	3
p-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, -5°C	p-ClC <sub>6</sub> H <sub>4</sub> HgCl (46)	3
o-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, -70°C, vigorous stirring	o-ClC <sub>6</sub> H <sub>4</sub> HgCl	12
p-EtOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, EtOH, -5°C	p-EtOC <sub>6</sub> H <sub>4</sub> HgCl (77)	3
p-EtO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, -10°C	p-EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> HgCl (45)	9
1-Naphthylamine	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, H <sub>2</sub> O, 0°C	1-Naphthyl HgBr (67)	8
o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, EtOAc, -15°C, vigorous stirring	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> HgCl (42)	12
o-PhC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, -60°C	o-PhC <sub>6</sub> H <sub>4</sub> HgCl (35)	6
2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(iii) NaNO <sub>2</sub> , H <sup>+</sup> (iv) HgCl <sub>2</sub> , Cu, HCl, MeCO, 0°C	2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> HgCl	9
1-Naphthylamine	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO (iii) aq NH <sub>3</sub>	bis(1-Naphthyl)Hg (53)	4

(continued)



Amine	Conditions <sup>a</sup>	Product (Yield, %) <sup>b</sup>	Ref.
p-IC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, Et <sub>2</sub> O, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO (iii) aq NH <sub>3</sub>	(p-IC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Hg (70)	4
	(iii) NaNO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub> (iv) Hg(SO <sub>4</sub> ), 180° (no Cu)	 Hg (98.5) <sup>d</sup>	13
	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, NH <sub>4</sub> OH	 Hg	14
	NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> , Cu <sub>2</sub> Cl <sub>2</sub>	 (33)	10
	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO	 HgCl	15

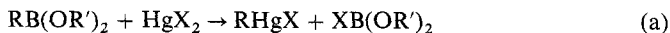
<sup>a</sup> Conditions: (i) for formation of double salt, (ii) for decomposition of double salt, (iii) for formation of diazonium salt, (iv) for direct formation of organomercurial from diazonium salt

<sup>b</sup> Yield calculated from isolated double salt.

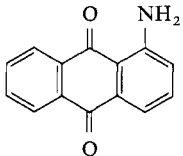
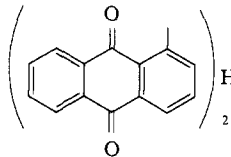
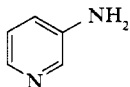
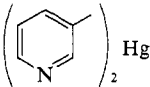
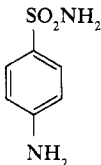
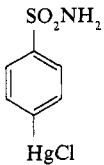
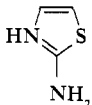
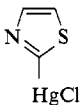
<sup>c</sup> Yield based on amine

#### 5.7.2.3.7. with Organosulfinic, Organosulfonic and Organoboronic Acid Derivatives.

(i) Mercurideboronations. Organoboronic acids, RB(OH)<sub>2</sub> or their esters with mercury salts HgX<sub>2</sub> [X = Cl, Br or OAc (OAc is OC(O)CH<sub>3</sub>)] provide<sup>1,2</sup> RHgX:



5.7. Formation of Bonds between Elements of Groups IVB and IIB 323  
 5.7.2. Carbon-Group-IIB Bonds  
 5.7.2.3. from Metal Salts

Amine	Conditions <sup>a</sup>	Product (Yield, %) <sup>b</sup>	Ref.
p-IC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	(i) NaNO <sub>2</sub> , HCl, Et <sub>2</sub> O, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO (iii) aq NH <sub>3</sub>	(p-IC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Hg (70)	4
	(iii) NaNO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub> (iv) Hg(SO <sub>4</sub> ), 180° (no Cu)	 Hg (98.5) <sup>d</sup>	13
	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO, NH <sub>4</sub> OH		14
	NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> , Cu <sub>2</sub> Cl <sub>2</sub>	 (33)	10
	(i) NaNO <sub>2</sub> , HCl, HgCl <sub>2</sub> (ii) Cu, Me <sub>2</sub> CO		15

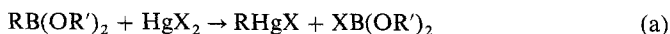
<sup>a</sup> Conditions: (i) for formation of double salt, (ii) for decomposition of double salt, (iii) for formation of diazonium salt, (iv) for direct formation of organomercurial from diazonium salt.

<sup>b</sup> Yield calculated from isolated double salt.

<sup>c</sup> Yield based on amine

5.7.2.3.7. with Organosulfinic, Organosulfonic and Organoboronic Acid Derivatives.

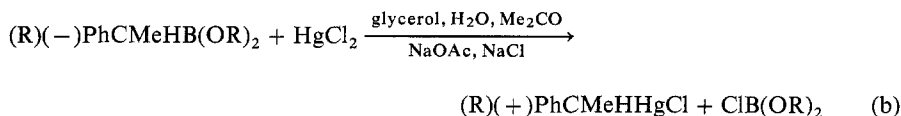
(i) Mercurideboronations. Organoboronic acids, RB(OH)<sub>2</sub> or their esters with mercury salts HgX<sub>2</sub> [X = Cl, Br or OAc (OAc is OC(O)CH<sub>3</sub>)] provide<sup>1,2</sup> RHgX:



where R = alkyl, vinyl or aryl; R' = H or alkyl. Similar reactions with HgO or Hg(NO<sub>3</sub>)<sub>2</sub> lead to R<sub>2</sub>Hg. Both H<sub>2</sub>O and organic media are used. This method of preparing organomercurials has only limited value for those boronic-acid derivatives obtained from organomagnesium halides or organolithiums, because the latter can be used directly to give the organomercurials. However, boronic acid derivatives can be obtained by other routes, e.g., by hydroboration of alkenes and alkynes, and so this method is important.

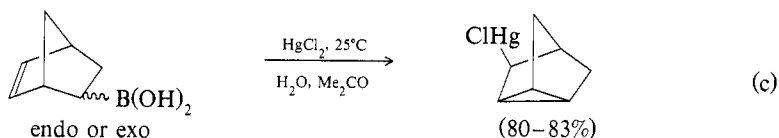
Diarylboronous acids, Ar<sub>2</sub>BOH, also react.

Alkylboronic acid derivatives retain configuration with Hg salts<sup>3</sup>, e.g.:



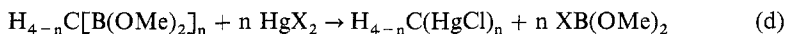
where R = H or n-Bu. The substitution of RCM<sub>2</sub>HB(OR')<sub>2</sub> proceeds by a concerted displacement mechanism<sup>3,4</sup>.

Reaction of exo- or endo-norbornen-2-boronic acid with HgCl<sub>2</sub> in aq Me<sub>2</sub>CO provides the rearranged 3-chloromercuritricyclo[2.2.1.0<sup>2,6</sup>]heptane<sup>5,6</sup>:

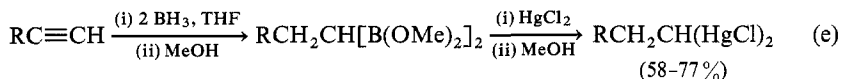


The exo-isomer is more reactive by a factor of 100.

Mercurideboronations occur with gem-di- and -polyboronate esters, e.g.<sup>7,8</sup>:

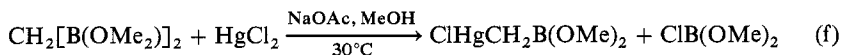


where X = OAc or Cl; n = 2–4. As gem-diboronate esters are available from hydroboration of alkynes:

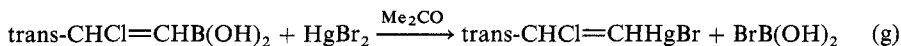


where R = n-Pr, n-Bu, t-Bu, n-Oct, or Ph; this provides a route to gem-dimercury alkanes<sup>9</sup>.

One B(OMe)<sub>2</sub> group can be cleaved from a gem-diboronate ester, e.g.<sup>10</sup>:

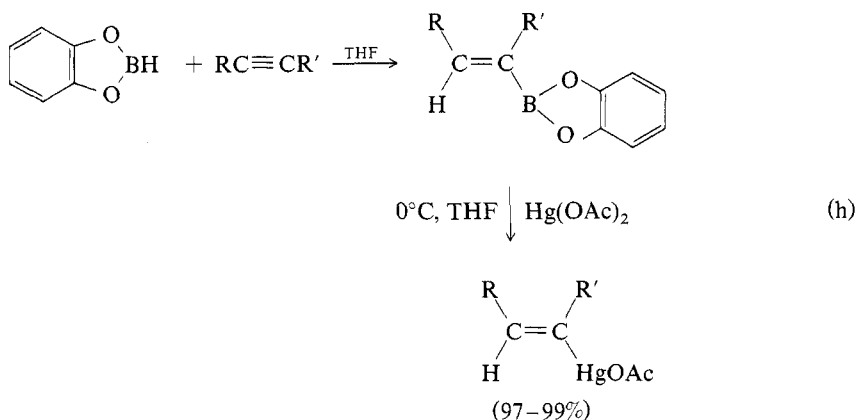


Mercurideboronation of vinylic boronic acid derivatives occurs with retention of configuration, e.g.<sup>11</sup>:



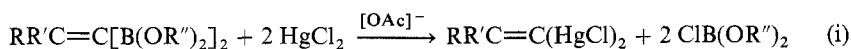
Because alkeneboronic esters are available from the cis-mono addition of HB(OR)<sub>2</sub> to alkynes, both internal and external compounds, a convenient route to isomerically pure

alkenylmercury chloride is available, e.g.<sup>12</sup>:

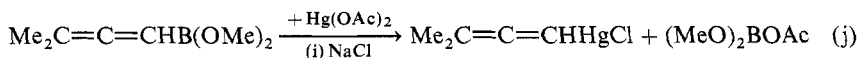


where R, R' = n-Pr, H; cylo-C<sub>6</sub>H<sub>11</sub>, H; Et, Et; t-Bu, Me; Cl(CH<sub>2</sub>)<sub>3</sub>, H.

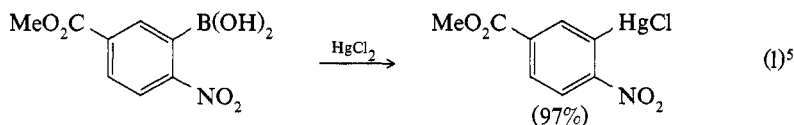
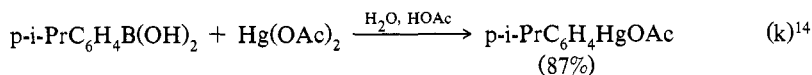
Alkene-1,1-diboronate esters also are reacted<sup>13</sup>:



where R''<sub>2</sub> = -(CH<sub>2</sub>)<sub>3</sub>- and R, R' (yield, %) = H, H (70); Et, Et (81); Ph, H (85); Me, Me (85); EtOCO, Me (80); -(CH<sub>2</sub>)<sub>5</sub>- (97); Me<sub>2</sub>C=CH, Me (74). Allenic derivatives also may be obtained<sup>14</sup>:



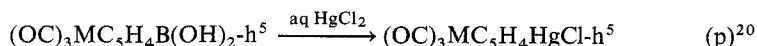
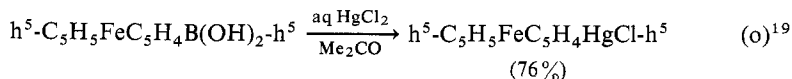
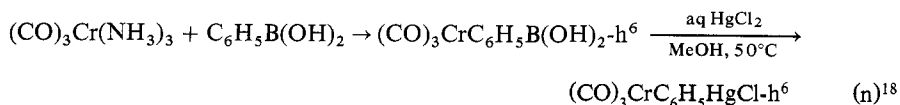
Substituted benzeneboronic acids undergo this reaction, e.g.:



As can be seen from reaction (l), these compounds can include groups that would be reactive toward organolithiums or organomagnesium halides and hence prohibit the use of such metal-Hg exchanges for their formation. Polycyclic aromatics<sup>6</sup>, heteroaromatics<sup>7</sup>:

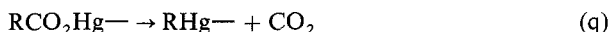


(where X = O or S) and transition-metal complexes containing aromatic ligands, e.g.:



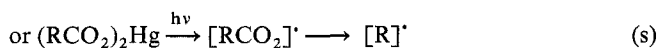
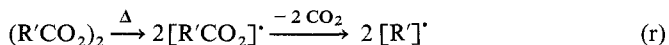
(where if M = Mn, the yield is 94% and if M = Re, the yield is 93%) also take part in these mercurideboronations.

(ii) Decarboxylations<sup>1,2</sup>. Decarboxylations of Hg carboxylates  $(\text{RCO}_2)_2\text{Hg}$  lead to C—Hg-bonded compounds. Two methods are employed; (a) UV- or free-radical-initiated reactions and (b) thermolysis:

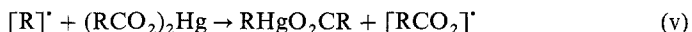


(iii) Photochemically or Radical-Initiated Decarboxylations<sup>21,22</sup>. Such decompositions of  $(\text{RCO}_2)_2\text{Hg}$  compounds lead to  $\text{RHgO}_2\text{CR}$  derivatives and proceed via free-radical chain mechanisms:

Initiation:

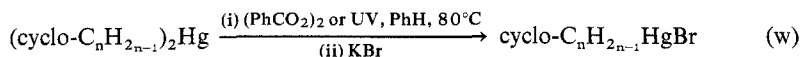


Propagation:

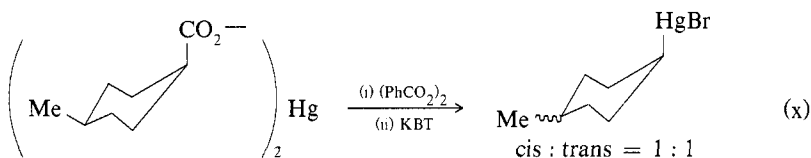


Acyl peroxides are used as initiators in refluxing benzene. The acyl peroxide used may be that derived from the carboxylate group of  $(\text{RCO}_2)_2\text{Hg}$  or, e.g.,  $(\text{PhCO}_2)_2$ . When the organic groups of the peroxide and carboxylate are different, it is possible for the organomercury product to be derived from the acyl peroxide, e.g., in the  $(\text{cyclo-C}_5\text{H}_9\text{CO}_2)_2\text{Hg}$ -( $\text{cyclo-C}_6\text{H}_{11}\text{CO}_2$ )<sub>2</sub> reaction<sup>23</sup>, but not in that of  $(\text{cyclo-C}_6\text{H}_{11}\text{CO}_2)_2\text{Hg}$ -( $\text{cyclo-C}_5\text{H}_9\text{CO}_2$ )<sub>2</sub>. The stability and rate of formation of all radicals taking part in the reaction are important in deciding the yields of major and minor products.

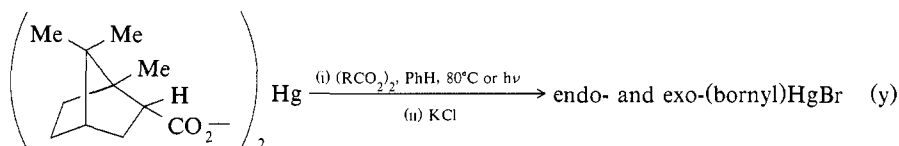
Alternatively, UV irradiation is used. Unactivated alkyl<sup>24,25</sup>, cycloalkyl<sup>26</sup> and aryl compounds, as well as o-carboranes participate<sup>27</sup>. Yields for the formation of methyl- and ethylmercurials from the carboxylates are 66 and 68%, respectively<sup>24</sup>:



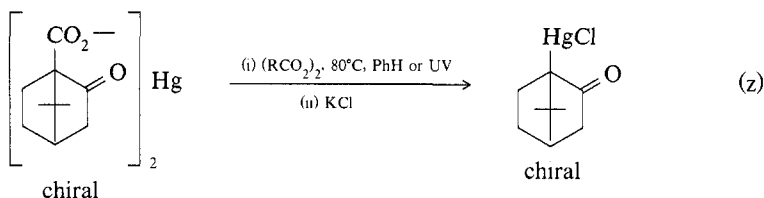
where  $n = 3-7, 11$  or  $12$ . Owing to the free-radical nature of the reaction, there is complete loss of configuration in the decarboxylation of Hg cis- or trans-4-methylcyclohexylcarboxylates<sup>28</sup>:



Another example of loss of configuration is the decarboxylation of chiral Hg endo-2-camphenecarboxylate<sup>22</sup>:

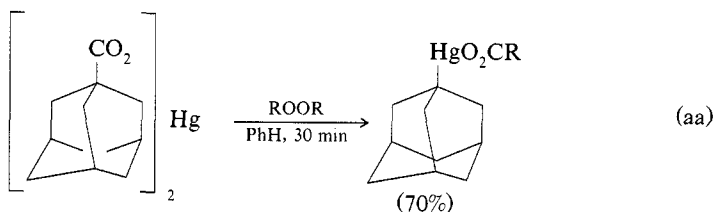


Although retention of configuration occurs in the decarboxylation of chiral Hg ketopinoate to the chiral 7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptylmercury compound<sup>22</sup>:



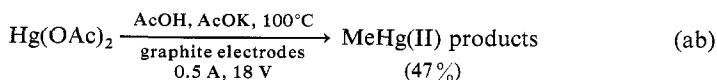
this is a consequence not of a different mechanism, but of the 7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptyl radical, as is found in other reactions, reacting in a stereospecific manner.

1-Adamantylmercury salts are obtained by decarboxylation, e.g.<sup>29</sup>:



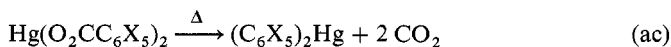
where R = 1-adamantyl.

Decarboxylation of  $\text{Hg}(\text{OAc})_2$  also is achieved electrolytically, e.g.<sup>30</sup>:

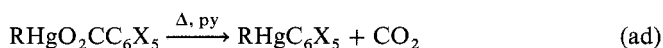


(iv) Thermal Decompositions<sup>31</sup>. Electronegative groups suppress free-radical decarboxylations; however, they promote thermal decarboxylations. Thermolyses are carried out neat on the molten (or melting) carboxylates or in polar solvents, such as pyridine (py), 1,2-dimethoxyethane (DME), H<sub>2</sub>O, or hexamethylphosphoramide (HMPA).

Mercury poly- and perhaloarene-carboxylates react. With Hg bis-pentahalobenzoates, e.g., good yields of (C<sub>6</sub>X<sub>5</sub>)<sub>2</sub>Hg are obtained:



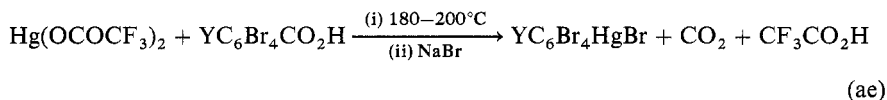
where, if X = F, at 210°C the yield<sup>32</sup> is 56%; if X = Cl, in hot py, the yield<sup>33</sup> is 80% and if X = Br, in hot py, the yield<sup>34</sup> is 60%. Unsymmetrical diorganomercurials are prepared from RHgO<sub>2</sub>CC<sub>6</sub>X<sub>5</sub>:



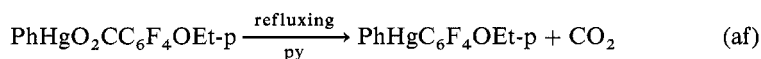
where if R = Ph, X = F<sup>32</sup>, Cl<sup>33</sup> or Br<sup>34</sup>; if R = Ph or p-MeC<sub>6</sub>H<sub>4</sub>, X = Cl<sup>33</sup> and if R = Me, X = F<sup>32</sup>. However, the two symmetrical diorganomercurials, R<sub>2</sub>Hg and (C<sub>6</sub>X<sub>5</sub>)<sub>2</sub>Hg, also can be formed.

In the presence of a chelating agent, L<sub>2</sub> [e.g., bipy (2,2'-bipyridyl), 1,10-phen-(1,10-phenanthroline), or diphos (1,2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)], Hg(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> provides<sup>32</sup> (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Hg·L<sub>2</sub> on thermolysis.

Thermolyses<sup>34</sup> work with (YC<sub>6</sub>Br<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Hg (Y = p-F, p-Cl or p-MeO) in py. For the compound with Y = p-Me, heating in py-nitrobenzene is required for formation of (YC<sub>6</sub>Br<sub>4</sub>)<sub>2</sub>Hg. The decarboxylation of YC<sub>6</sub>Br<sub>4</sub>CO<sub>2</sub>H (Y = o-Me or m-MeO) (and formation of organomercurials) is effected<sup>34</sup> at 180–200°C in molten Hg(OCOCF<sub>3</sub>)<sub>2</sub>, e.g.:



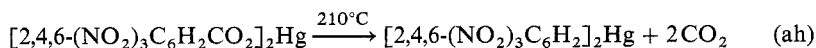
The compound, PhHgO<sub>2</sub>CC<sub>6</sub>F<sub>4</sub>OEt-p, is decarboxylated in boiling py<sup>35</sup>:



Formation of bis-2-perfluoropyridylmercury also is achieved by decarboxylation<sup>36</sup>:



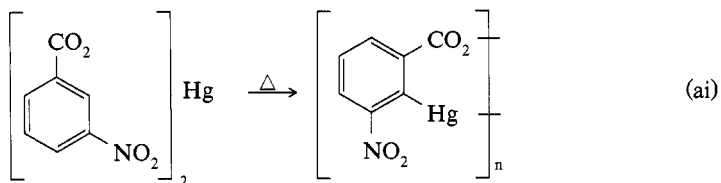
Mercury bis(2,4,6-trinitrobenzoate) can be thermolyzed to a diarylmercurial<sup>37</sup>:



**Vigorous decomposition of [3,5-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>]<sub>2</sub>Hg to carbon and Hg at 175°–200°C under vacuum.**

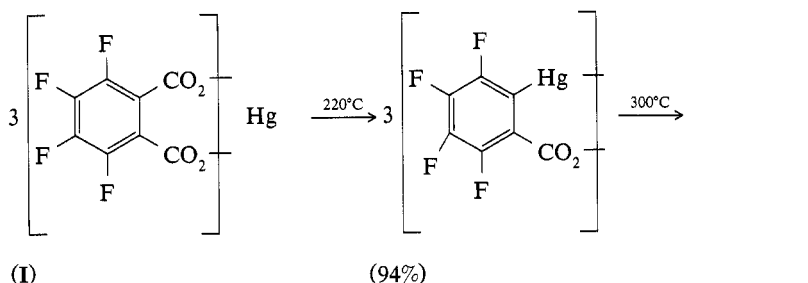
Although decarboxylation of (o-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>Hg at 180°C provides<sup>38</sup> some (o-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg (16%) the meta and para isomers on heating are metallated ortho to

the carboxylate group, e.g.:

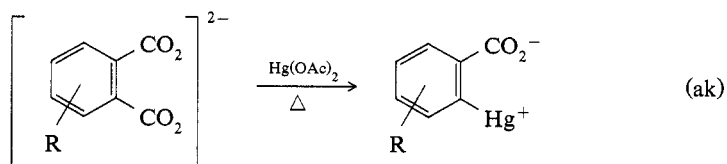


Decarboxylation of  $(2,6\text{-F}_2\text{C}_6\text{H}_3\text{CO}_2)_2\text{Hg}$  in refluxing DMSO provides  $(2,6\text{-F}_2\text{C}_6\text{H}_3)_2\text{Hg}$  in 40% yield; the other 2,6-dihalo derivatives do not decarboxylate so readily<sup>39</sup>.

The Hg salt of tetrafluorophthalic acid (I) is decarboxylated partially at 220°C and completely<sup>40</sup> at 300°C to dodecafluorotribenzo-1,4,7-trimercuracyclononatriene:



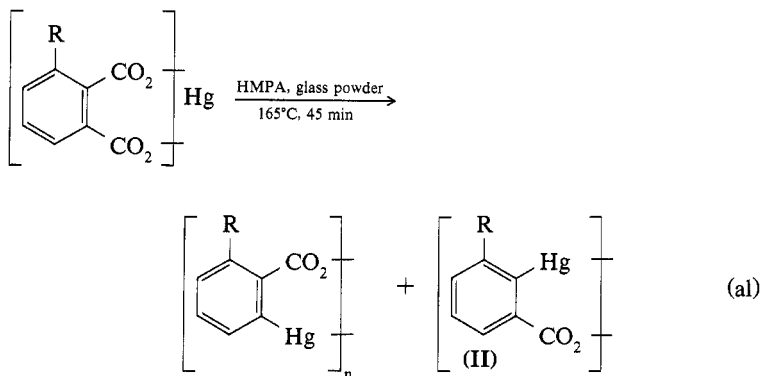
Reactions of o-dicarboxylates with  $\text{Hg}(\text{OAc})_2$  result<sup>31</sup> in loss of one  $\text{CO}_2$  group:



where  $\text{R} = \text{H}$  (yield, 85%)<sup>41</sup>,  $3\text{-Cl}$ <sup>42</sup>,  $3\text{-Br}$ <sup>42</sup>,  $3\text{-NO}_2$ <sup>41</sup>,  $3\text{-CO}_2\text{H}$ <sup>43</sup> or  $4\text{-NO}_2$ <sup>37</sup>.

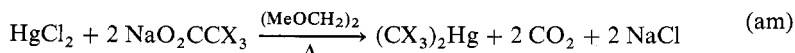


Good yields are also obtained on heating in HMPA, especially when soft glass powder is present, e.g.:



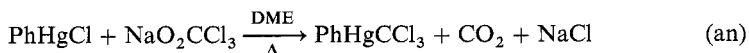
where if  $\text{R} = \text{NO}_2$  the product ratio is 1 : 3 and if  $\text{R} = \text{Me}$  the product ratio is 12 : 5; for  $\text{R} = \text{Cl}$ , only (II) ( $\text{R} = \text{Cl}$ ) is found<sup>44</sup>.

Both  $(\text{Cl}_3\text{C})_2\text{Hg}$ <sup>45</sup> and  $(\text{Br}_3\text{C})_2\text{Hg}$ <sup>46</sup> are prepared by decarboxylation on heating in DME, e.g.



but Hg trifluoroacetate only undergoes monodecarboxylation<sup>47</sup> at  $\leq 300^\circ\text{C}$  to give  $\text{CF}_3\text{HgOCOCF}_3$ . However, formation of  $(\text{CF}_3)_2\text{Hg}$  is achieved at  $200^\circ\text{C}$  if  $\text{K}_2\text{CO}_3$ <sup>48</sup> or a bidentate ligand, e.g., 1,10-phen or bipy<sup>49</sup>, is present.

Organomercury(trihalomethyl) compounds also may be prepared<sup>45</sup> by this route, e.g.:

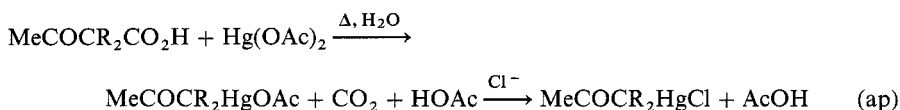


Compounds,  $(\text{C}_2\text{F}_5)_2\text{Hg}$ ,  $(\text{C}_3\text{F}_7)_2\text{Hg}$ ,  $(\text{C}_3\text{H}_7\text{CF}=\text{CF})_2\text{Hg}$ <sup>50</sup>, and  $(\text{CFCINO}_2)_2\text{Hg}$ <sup>51</sup> also are obtained by decarboxylations of the appropriate biscarboxylates.

Bis(2-oxo-2,2-dialkylpropyl)mercurials are obtained by thermolysis of Hg salts of  $\alpha,\alpha$ -dialkylacetoacetic acids, e.g.<sup>52</sup>:



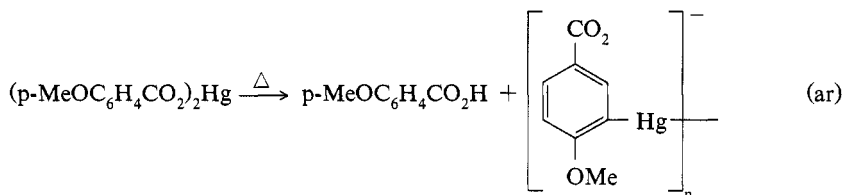
where  $\text{R} = \text{Me}$  or  $\text{Et}$ . Modification leads to the formation of  $\text{MeCOCR}_2\text{HgCl}$ :



Benzoylactic acid reacts<sup>52</sup> with HgO in  $\text{H}_2\text{O}$ , e.g.:

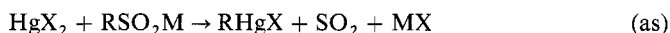


The most serious side reactions are mercurations, e.g., with Hg *m*-nitrobenzoates, Eq. (ai), or<sup>52</sup>:



The absence of free hydrogens in the aromatic ring, especially in positions ortho to the  $\text{—CO}_2\text{Hg—}$  group, prevents or limits mercurations, as do electronegative groups in the aromatic ring.

(v) **Desulfinations.** Thermal desulfinations of organosulfinic acids or salts with  $\text{HgX}_2$  produces organomercurials under mild conditions:

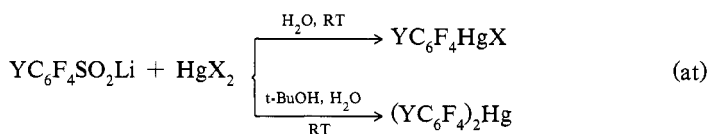


where if  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{OAc}$ ;  $\text{R} = \text{alkyl}$  or  $\text{aryl}$ ;  $\text{M} = \text{H}, \text{Na}$  or  $\text{Li}$ .

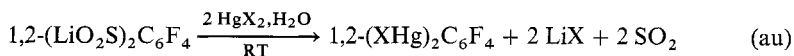
Mixing the sulfinic acid and  $\text{HgX}_2$  in  $\text{H}_2\text{O}$  or alcohol and heating the resulting suspension at  $80\text{--}100^\circ\text{C}$  may be required<sup>54</sup>, but modifications involve the alkali-metal salts of sulfinic acids<sup>55–57</sup> or performed organosulfinate mercurials<sup>58–60</sup>. Solvents, such as dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidine and *py*, are used also (see Table 1).

Reactions between  $\text{RSO}_2\text{M}$  ( $\text{M} = \text{H}, \text{Li}, \text{Na}, \text{K}$ , etc.) and  $\text{HgX}_2$  proceed via formation of  $\text{RSO}_2\text{HgX}$  intermediates,<sup>58,59</sup> which, when isolated, decompose on heating to  $\text{RHgX}$ .

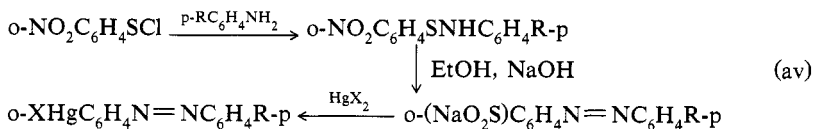
Electronegative substituents promote the reaction; e.g., desulfination of  $\text{YC}_6\text{F}_4\text{SO}_2\text{Li}$  with  $\text{HgX}_2$  proceeds at  $\text{RT}$ <sup>56</sup>. Either mono- or diorganomercurials can be obtained:



where  $\text{Y} = \text{F}$ , *o*-, *m*- or *p*- $\text{H}$ ;  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{OAc}$ . Perfluoro-*o*- and *p*-disulfates also react, e.g.:

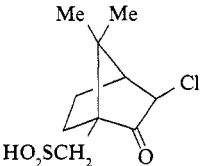
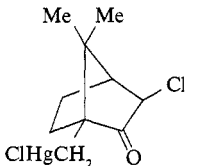


The desulfination route to organomercurials also is shown, e.g.<sup>69</sup> in:

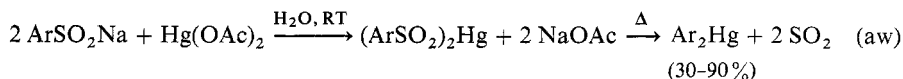


where  $\text{R} = \text{H}, \text{Me}, \text{OMe}$  or  $\text{Cl}$ .

TABLE 1. ORGANOMERCURIALS FROM ORGANOSULFINIC ACIDS OR THEIR DERIVATIVES WITH MERCURY SALTS

Sulfinic acid or derivative	Reaction conditions	Product (yield, %)	Ref.
MeSO <sub>2</sub> Na	HgCl <sub>2</sub> , EtOH	MeHgCl	1
C <sub>6</sub> H <sub>13</sub> SO <sub>2</sub> HgCl	Δ	C <sub>6</sub> H <sub>13</sub> HgCl (58)	58
C <sub>12</sub> H <sub>25</sub> SO <sub>2</sub> Na	HgCl <sub>2</sub> , H <sub>2</sub> O, 2 h	C <sub>12</sub> H <sub>25</sub> HgCl (49)	57
cyclo-C <sub>6</sub> H <sub>11</sub> SO <sub>2</sub> HgCl	Δ	cyclo-C <sub>6</sub> H <sub>11</sub> HgCl (45)	58
 HO <sub>2</sub> SCH <sub>2</sub>	HgCl <sub>2</sub> , py Δ, 3 h	 ClHgCH <sub>2</sub> (40–50 %)	61
(PhSO <sub>2</sub> ) <sub>2</sub> Hg	115°C, 1, h	Ph <sub>2</sub> Hg (84)	60
p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Na	HgCl <sub>2</sub> , H <sub>2</sub> O, 2 h	p-MeC <sub>6</sub> H <sub>4</sub> HgCl (51–57)	55
p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Na	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, Δ	(p-MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Hg (25)	60
p-ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Hg(OAc) <sub>2</sub> , AcOH, Δ, 15 min	p-ClC <sub>6</sub> H <sub>4</sub> HgOAc (70)	62
p-ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> HgCl	100–200°C	p-ClC <sub>6</sub> H <sub>4</sub> HgCl (40)	59
p-ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Na	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, Δ	p-ClC <sub>6</sub> H <sub>4</sub> HgO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Cl-p (21)	60
p-FC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Na	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, 100°C	(p-FC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Hg (16)	60
(p-FC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> ) <sub>2</sub> Hg	110–140°C, 6 h	(p-FC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> Hg (90)	60
o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	HgCl <sub>2</sub> , Et <sub>2</sub> O, H <sub>2</sub> O	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> HgCl (78)	63
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Li	Hg(OAc) <sub>2</sub> , H <sub>2</sub> O, RT	C <sub>6</sub> F <sub>5</sub> HgOAc	56
C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> Li	HgCl <sub>2</sub> , t-BuOH, H <sub>2</sub> O, RT	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Hg	56
(2,3,4-Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> Hg	120–180°C, 1 h	(2,3,4-Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> Hg (42)	60
m-(NaO <sub>2</sub> S) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	HgCl <sub>2</sub> , H <sub>2</sub> O, Δ	(m-ClHg) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (82)	64
m-(KO <sub>2</sub> S) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Hg(OAc) <sub>2</sub> , HOAc, Δ, 2 h	m-(AcOHg) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (70)	65
o-C <sub>6</sub> H <sub>4</sub> NSO <sub>2</sub> Na	HgCl <sub>2</sub> , H <sub>2</sub> O	o-Pyridyl HgCl	66
(8-Quinolyl-SO <sub>2</sub> ) <sub>2</sub> Hg	130–170°C, 1 h	(8-Quinolyl) <sub>2</sub> Hg (42)	60
h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> SO <sub>2</sub> Na-h <sup>5</sup>	HgCl <sub>2</sub> , EtOH, RT	h <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> HgCl (ca. 100)	67
(CO) <sub>3</sub> MnC <sub>5</sub> H <sub>4</sub> SO <sub>2</sub> Na-h <sup>5</sup>	HgBr <sub>2</sub>	(CO) <sub>3</sub> MnC <sub>5</sub> H <sub>4</sub> HgBr	68

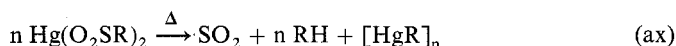
Preformed and isolated Hg bis(arenesulfinates), prepared from Hg(OAc)<sub>2</sub> and ArSO<sub>2</sub>Na in AcOH, are thermolyzed<sup>60</sup> in sublimers, on heating in solution or even on melting<sup>60</sup>:



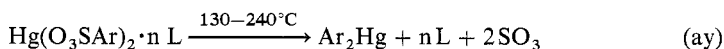
where Ar = p-YC<sub>6</sub>H<sub>4</sub>; Y = H, Me, Br, Cl or F; 2,3,6- or 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; 2-naphthyl or 8-quinolyl. Alternatively, (ArSO<sub>2</sub>)<sub>2</sub>Hg can be heated<sup>60</sup> in H<sub>2</sub>O, either Ar<sub>2</sub>Hg or ArHgO<sub>2</sub>SAr is formed, depending on substituents; e.g., Ar<sub>2</sub>Hg is formed with Ar = p-YC<sub>6</sub>H<sub>4</sub> (Y = H, Me, F or MeCONH), 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,4,6-i-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> or 8-quinolyl; ArHgO<sub>2</sub>SAr is formed with Ar = p-XC<sub>6</sub>H<sub>4</sub> (X = Cl or Br), 2,3,4-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub> or 2-naphthyl.

Comparison of the yields from reactions of  $\text{ArSO}_2\text{Li}$  and  $\text{HgX}_2$  with thermolysis of preformed  $(\text{ArSO}_2)_2\text{Hg}$  show the latter to be the better; cf. reaction of p-fluorobenzene-sulfinate systems in Table 1.

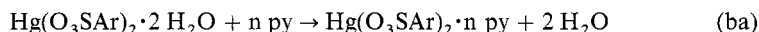
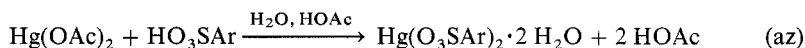
These desulfonations are not stereoselective. Either exo- or endo-norbornylsulfinate-mercury chloride, on heating in DME at  $100^\circ\text{C}$ , provides exo-norbornylmercury chloride<sup>58</sup> (39% yield). Another example is that of erythro-t-BuCHDCHDSO<sub>2</sub>HgCl, which gives an equimolar mixture of threo- and erythro-t-BuCHDCHDHgCl on heating<sup>58</sup>.



(vi) **Desulfonations**<sup>63,64</sup> Thermal decomposition of Hg bis(arenesulfonate) complexes  $\text{Hg}(\text{O}_3\text{SAr})_2 \cdot n \text{L}$  (Ar = polyhalophenyl, L =  $\text{H}_2\text{O}$  or py, also can produce  $\text{Ar}_2\text{Hg}$ :



The preparations of  $\text{Hg}(\text{O}_3\text{SAr})_2 \cdot n \text{L}$  are:



Better yields of  $\text{Ar}_2\text{Hg}$  are obtained from the pyridine complexes than from the hydrates; lower T also can be used, suggesting some assistance by py. ortho-Mercuration of  $\text{Hg}(\text{O}_3\text{SC}_6\text{X}_4\text{H-o})_2$  (X = F or Cl) competes; such pyridinates provide no  $\text{Ar}_2\text{Hg}$  on thermolysis (see Table 2).

TABLE 2. THERMAL DECOMPOSITION OF  $\text{Hg}(\text{O}_3\text{SAr})_2$  COMPLEXES<sup>a</sup>

Compound	Yield of $\text{Ar}_2\text{Hg}$ (%)	Other Mercury Products
$(\text{C}_6\text{Cl}_5\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	81	
$(\text{C}_6\text{Cl}_5\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	64	
$(\text{p-HC}_6\text{Cl}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	86	
$(\text{p-HC}_6\text{Cl}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	78	
$(\text{m-HC}_6\text{Cl}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	86	
$(\text{m-HC}_6\text{Cl}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	44	
$(\text{o-HC}_6\text{Cl}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	—	$[-\text{HgC}_6\text{Cl}_4\text{SO}_3-]_n$ (56%)
$(\text{o-HC}_6\text{Cl}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	—	$[-\text{o-HgC}_6\text{Cl}_4\text{SO}_3-]_n$ + $\text{o-(o-HC}_6\text{Cl}_4\text{SO}_3\text{Hg})_2\text{C}_6\text{Cl}_4$
$(\text{C}_6\text{F}_5\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	73	
$(\text{C}_6\text{F}_5\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	53	
$(\text{p-HC}_6\text{F}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	60	
$(\text{p-HC}_6\text{F}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	17	$\text{p-(p-HC}_6\text{F}_4\text{SO}_3\text{Hg})_2\text{C}_6\text{F}_4$
$(\text{m-HC}_6\text{F}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	45	$[-\text{m-HgC}_6\text{F}_4\text{SO}_3-]_n$ (25%)
$(\text{m-HC}_6\text{F}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	—	$[-\text{m-HgC}_6\text{F}_4\text{SO}_3-]_n$ and $\text{m-HC}_6\text{F}_4\text{HgO}_3\text{SC}_6\text{F}_4\text{H-m}$
$(\text{o-HC}_6\text{F}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{py}$	—	$[-\text{o-HgC}_6\text{F}_4\text{SO}_3-]_n$ ca. 100%
$(\text{o-HC}_6\text{F}_4\text{SO}_3)_2\text{Hg} \cdot 2 \text{H}_2\text{O}$	—	$[-\text{o-HgC}_6\text{F}_4\text{SO}_3-]_n$

<sup>a</sup> Refs. 71 and 72.

Reactions of the dihydrates, although leading to  $\text{Ar}_2\text{Hg}$ , do provide considerable yields of products of hydrolysis, hydrolytic desulfonation and mercuration, e.g.,  $\text{-(Hg-C}_6\text{X}_4\text{SO}_3\text{)}_n$  or  $(\text{HC}_6\text{X}_4\text{SO}_3\text{Hg})_2\text{C}_6\text{X}_4$  species. More mercuration products are found for polyfluoro- than for polychlorophenyl derivatives.

Electronegative groups in the aromatic are necessary for reaction; the polyhalo groups deactivate the aromatic for electrophilic substitution by  $\text{SO}_3$ , increase the thermal stability and also block potential sites of substitution.

(J. L. WARDELL)

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#### 5.7.2.4. from Other Group-IIB Organometallics of the Same Metal

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### 5.7.2. Carbon-Group-IIB Bonds

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#### 5.7.2.4. from Other Group-IIB Organometallics of the Same Metal

Organo-Zn, -Cd and -Hg derivatives can be prepared from other compounds by proton-metal exchange with acidic hydrocarbons by olefin insertion and by metal-metal exchange with other organometallics. In all cases alkyl groups are substituted by other

alkyl, alkenyl, alkynyl or aryl groups. The simple dimethyl or diethyl Zn and Cd compounds are starting materials for these reactions, which are used to prepare special organo-Zn and -Cd compounds. Because Hg—C bonds have low reactivity, few corresponding reactions of alkyl Hg compounds are possible.

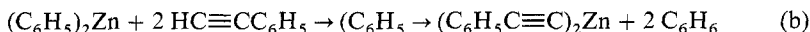
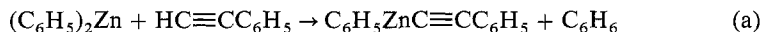
In reactions of organo-Zn and -Cd compounds, O<sub>2</sub> and moisture must be excluded. Therefore, all operations must be performed under Ar, in pure N<sub>2</sub> or in vacuum. Some R<sub>2</sub>Zn and most R<sub>2</sub>Cd compounds decompose at RT. In these cases the compounds must be prepared and stored at <0°C.

Most R<sub>2</sub>M compounds of Zn and Cd enflame spontaneously in air or are oxidized or hydrolyzed rapidly. Furthermore, volatile R<sub>2</sub>Cd and R<sub>2</sub>Hg derivatives are poisons. Therefore, these compounds must be handled with caution.

(K.-H. THIELE)

#### 5.7.2.4.1. by Proton–Metal Exchange with Acidic Hydrocarbons.

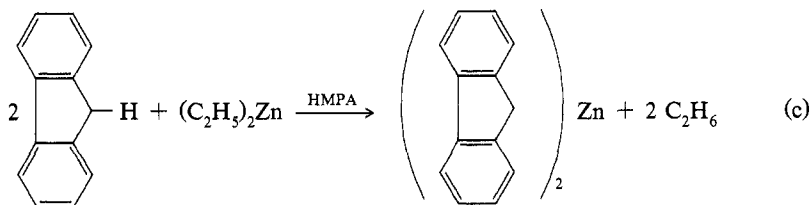
The R<sub>2</sub>Zn compounds react with acidic hydrocarbons to split the original Zn—C bonds and form new ones. The rate depends on hydrocarbon acidity; e.g., reactions with triphenylmethane proceed slowly and incompletely. Therefore, it is nearly impossible to obtain organozincs with stoichiometric compositions. More definite results are obtained with 1-alkynes, in which, depending on the molar ratio, one or two organic groups at Zn can be substituted for alkynyl groups<sup>1</sup>:



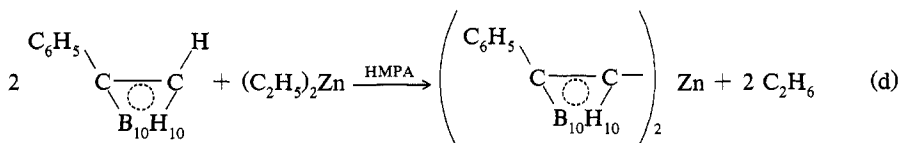
The reactions are carried out in Et<sub>2</sub>O or liq NH<sub>3</sub> at low T.

Zinc dialkyls do not react with phenylacetylene in Et<sub>2</sub>O but do so in more strongly polar aprotic solvents. The reaction half-lives decrease with increasing donor power of solvent, e.g., in reaction (b) with  $\tau/2$  values of 270 in N,N-dimethylformamide (DMF), 200 in dimethylsulfoxide (DMSO) and < 8 s in hexamethylphosphoramide (HMPA)<sup>2</sup>.

In HMPA (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn also reacts with less acidic hydrocarbons, such as fluorene:



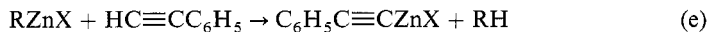
or carboranes:





However, strong donors used as solvents give  $R_2Zn \cdot 2D$  complexes that cannot be liberated from the donor molecules without decomposition.

Alkylzinc halides react with 1-alkynes in a similar way. The electronegative substituent, X, causes a higher polarity of the  $Zn-C$  bonds in  $RZnX$  compounds. Therefore, phenylethynylzinc halides can be synthesized even in nonpolar or weakly polar solvents, such as benzene, toluene or  $Et_2O$  with satisfactory rates in yields of 40–70%<sup>3</sup>:



where  $R = C_2H_5$ ,  $CH_2=CHCH_2$ . The reactivity of  $RZnX$  compounds with nucleophilic agents decreases  $C_2H_5ZnI > CH_2=CHCH_2ZnBr > C_2H_5ZnCl$ .

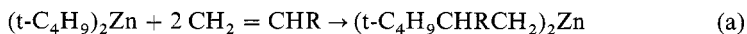
Alkynylzinc halides yield alkynyl ketones, which are otherwise difficult to obtain. With acid chlorides they give yields of 30–70%.

(K.-H. THIELE)

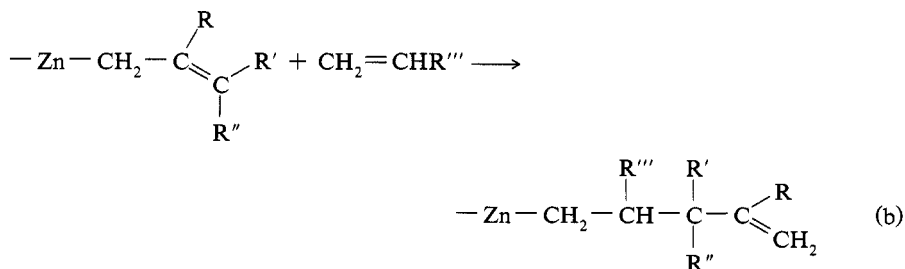
1. R. Nast, O. Künzel, R. Müller, *Chem. Ber.*, **95**, 2155 (1962).
2. O. Yu. Okhlobystin, L. I. Zakharkin, *J. Organomet. Chem.*, **3**, 257 (1965).
3. L. I. Vereshchagin, *J. Org. Chem., USSR (Engl. Transl.)* **2**, 1895 (1966).

#### 5.7.2.4.2. by Olefin Insertion.

The  $Zn-C$  bonds of  $R_2Zn$  compounds only slowly and incompletely react with alkenes, with the exception of  $(t-C_4H_9)_2Zn$  which can add 2 mol of alk-1-enes<sup>1</sup>. The insertion of ethylene results in bis(3,3-dimethylbutyl)zinc in 94% yield. With other alk-1-enes the Zn atom is attached preferentially to the C-2 atom:



Zinc dialk-2-enyls are more reactive than zinc dialkyls; e.g., diallylzincs react in toluene with 10–20 MPa ethylene at RT in 1–4 days to give the corresponding zinc dialk-4-enyls<sup>2</sup>. When other 1-alkenes are used the Zn is added regioselectively to the C-1 atoms of two alkenes:



Under these conditions, alkynes are not inserted into the  $Zn-C$  bonds. Donors decrease the rate.

5.7. Formation of Bonds between Elements of Groups IVB and IIB 337  
 5.7.2. Carbon-Group-IIB Bonds  
 5.7.2.4. from Other Group-IIB Organometallics of the Same Metal

However, strong donors used as solvents give  $R_2Zn \cdot 2D$  complexes that cannot be liberated from the donor molecules without decomposition.

Alkylzinc halides react with 1-alkynes in a similar way. The electronegative substituent, X, causes a higher polarity of the  $Zn-C$  bonds in  $RZnX$  compounds. Therefore, phenylethynylzinc halides can be synthesized even in nonpolar or weakly polar solvents, such as benzene, toluene or  $Et_2O$  with satisfactory rates in yields of 40–70%<sup>3</sup>:



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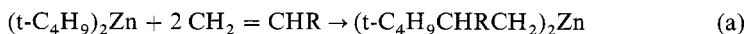
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(K.-H. THIELE)

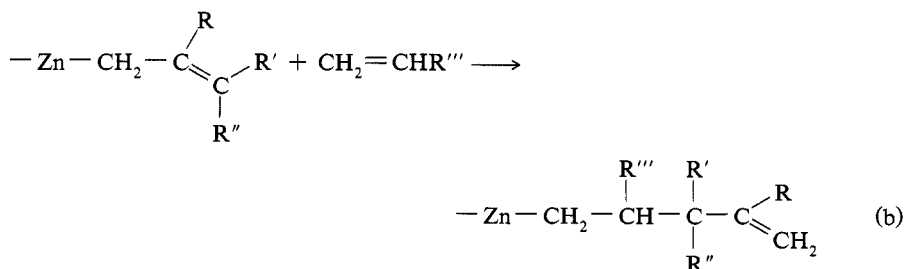
1. R. Nast, O. Künzel, R. Müller, *Chem. Ber.*, **95**, 2155 (1962).
2. O. Yu. Okhlobystin, L. I. Zakharkin, *J. Organomet. Chem.*, **3**, 257 (1965).
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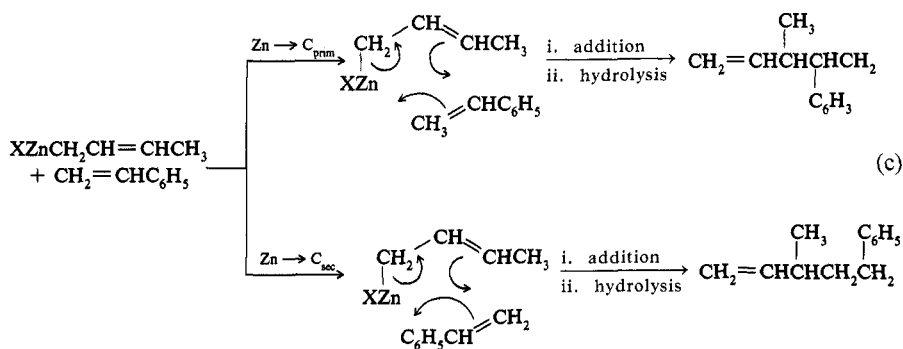
Zinc dialk-2-enyls are more reactive than zinc dialkyls; e.g., diallylzincs react in toluene with 10–20 MPa ethylene at RT in 1–4 days to give the corresponding zinc dialk-4-enyls<sup>2</sup>. When other 1-alkenes are used the Zn is added regioselectively to the C-1 atoms of two alkenes:



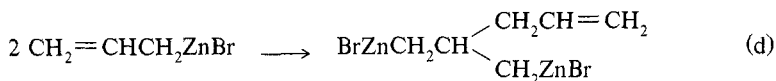
Under these conditions, alkynes are not inserted into the  $Zn-C$  bonds. Donors decrease the rate.

Cyclic olefins with internal disubstituted C=C bonds react with zinc dialk-2-enyls at  $-20^{\circ}\text{C}$  to  $-5^{\circ}\text{C}$  even under atm P. With 3,3-dimethylcyclopropene in ether, a stereo-regular cis addition occurs forming bis[2,2-dimethyl-3(Z)-alk-2-enyl]cyclopropyl] derivatives<sup>2</sup>.

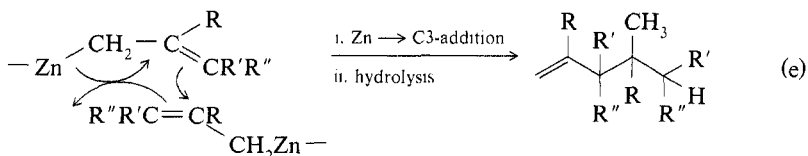
The  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{ZnX}$  compounds ( $\text{X} = n\text{-C}_4\text{H}_9, t\text{-C}_4\text{H}_9, \text{C}_6\text{H}_5, \text{C}_6\text{H}_{11}, \text{Cl}, \text{OCH}_3, \text{OC}_6\text{H}_5$ ) behave like the zinc dialkenyls with styrene. The Zn atom is attached regioselectively to the primary (prim) or secondary (sec) carbon atom, depending on the inductive effect of X. The  $\text{Zn}-\text{C}_{\text{prim}}$  addition is favored by electron-attracting substituents. The  $\log (\text{Zn} \rightarrow \text{C}_{\text{prim}} / \text{Zn} \rightarrow \text{C}_{\text{sec}})$  ratio depends<sup>3</sup> linearly on the polar substituent constants of X.



The alkenyl double bonds of allylzincs can also react with their own Zn—C bonds in a  $\text{Zn} \rightarrow \text{C}-3$  addition, e.g., in the intramolecular dimerization of allylzinc bromide<sup>4</sup>:



Corresponding reactions are also known with Zn dialk-2-enyls<sup>5</sup>:



where R, R' or R'' = H, CH<sub>3</sub>. The resulting oligomeric organozincs cannot be distilled and, therefore, cannot be isolated pure. Hydrolysis yields the corresponding olefins.

These reactions are mainly for the synthesis of special alkenes.

(K.-H. THIELE)

1. H. Lehmkuhl, O. Olbrych, *Justus Liebigs Ann. Chem.*, 1162 (1975).
2. H. Lehmkuhl, I. Döring, H. Nehl, *J. Organomet. Chem.*, 221, 123 (1981).
3. H. Lehmkuhl, H. Nehl, *J. Organomet. Chem.*, 221, 131 (1981).
4. G. Courtois, L. Miginiac, *J. Organomet. Chem.*, 52, 241 (1973).
5. H. Lehmkuhl, I. Döring, H. Nehl, *J. Organomet. Chem.*, 221, 7 (1981).

## 5.7. Formation of Bonds between Elements of Groups IVB and IIB 339

## 5.7.2. Carbon-Group-IIB Bonds

## 5.7.2.4. from Other Group-IIB Organometallics of the Same Metal

**5.7.2.4.3. by Metal-Metal Exchange with Other Organometallics.**

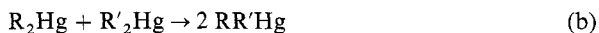
Different  $R_2M$  compounds react by metal-metal exchange to form  $RR'M$  derivatives. Such reactions yield unsymmetrical Zn diorganyls:



Reactions (a) are equilibria. Low  $T$  favors the formation of the unsymmetrical Zn diorganyls. At higher  $T$ , the reactions reverse. No solvent is required, but hydrocarbons may be used with solid Zn diaryls. Polar solvents such as  $Et_2O$  diminish the rate, and it is difficult to remove the donor from the  $RR'Zn$  derivatives completely. Details of reactions with  $R = CH_3CH=CHCH_2$  and  $R' = n-C_4H_9$ ,  $t-C_4H_9$ ,  $C_6H_5$  and cyclo- $C_6H_{11}$  are available<sup>1</sup>. The reactions are carried out at RT with the exception of the unstable  $t-C_4H_9$  derivative, which requires  $-40^\circ C$ . The mixed Zn diorganyls are obtained nearly quantitatively.

The corresponding  $RR'Cd$  compounds are synthesized similarly, but there is no information about the isolation of pure compounds.

Distributions of the type:

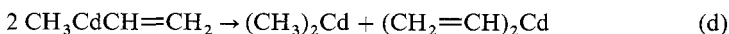


are suitable for the synthesis of mixed Hg diorganyls. The rate of formation and the stability of  $RR'Hg$  compounds against exchange of the substituents increases with the electronegativity of the organic groups. The equilibrium constants for  $R = C_nH_{2n+1}$  are 4 ( $R' = C_nH_{2n+1}$ ), ca. 100 ( $R' =$  alkenyl and cyclopropyl groups) and  $>100$  ( $R' = C_nF_{2n+1}$ ).

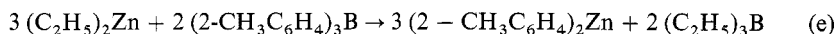
A similar reaction takes place between  $(CH_3)_2Cd$  and  $(CH_2=CH)_2Hg$ , but only one of each organic group is exchanged<sup>2</sup>:



Methylvinylmercury is stable at RT, but the corresponding mixed Cd compound disproportionates under the same conditions, forming the symmetrical dialkyls:



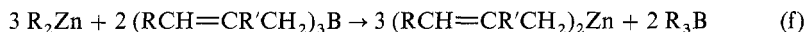
Simple dialkyls of Zn and Cd react with boron triorganyls by metal-metal exchange. No solvent is necessary; e.g., heating a mixture of dimethyl- or diethylzinc with  $(2-CH_3C_6H_4)_3B$  releases  $Et_3B$ , and the reaction is complete in a few hours<sup>3</sup>:



Other Zn diaryls can be prepared in the same manner with nearly quantitative yields, but the well-known syntheses from Zn chloride and arylmagnesium halides are more convenient and are preferred.

Diethyl- or dimethylzinc with  $(C_6H_5CH_2)_3B$  yields pure, noncomplexed,  $(C_6H_5CH_2)_2Zn$ , which cannot be prepared in any other way<sup>3</sup>. The reaction with diethylzinc runs faster at  $80^\circ C$  than with the low-mp  $Me_2Zn$  at  $50^\circ C$ , but the purity of  $(C_6H_5CH_2)_2Zn$  is better when prepared at lower  $T$ .

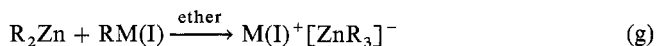
Reactions of simple zinc dialkyls and boron triallyls at RT:



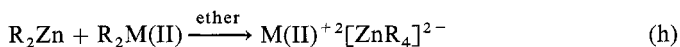
allow the synthesis of zinc diallyls, which cannot be prepared pure by other methods<sup>4,5</sup>. The alkyl-allyl exchange takes place in seconds and resembles an ionic reaction. Using  $\text{Me}_2\text{Zn}$  as starting material, pure allylzincs are obtained, because the volatile  $\text{Me}_3\text{B}$  evaporates completely from the mixture.

Cadmium diallyls are also formed immediately on adding boron triallyls to  $\text{Me}_2\text{Cd}$ <sup>6</sup>. Because of the low T decomposition of the allylcadmiums, the reactions must be performed at ca.  $-20^\circ\text{C}$ .

Complex formation of the type:



where  $\text{M}(\text{I}) = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ , and:



where  $\text{M}(\text{II}) = \text{Ca}, \text{Sr}, \text{Ba}$ , in  $\text{Et}_2\text{O}$  may be regarded as a special kind of metal-metal exchange. Whereas  $\text{M}_2(\text{I})[\text{Zn}(\text{C}\equiv\text{CH})_4]$  complexes<sup>7</sup> consist of ions, there exist organic group bridges between the metal atoms for  $\text{M}(\text{II})[\text{Zn}(\text{C}_2\text{H}_5)_4]$  derivatives<sup>8,9</sup>, of<sup>10</sup>  $\text{Li}_2[\text{Zn}(\text{CH}_3)_4]$ , of<sup>11</sup>  $\text{Li}[\text{Zn}(\text{C}_6\text{H}_5)_3]$  and of<sup>11</sup>  $\text{Na}[\text{Zn}(\text{C}_6\text{H}_5)_2\text{C}(\text{C}_6\text{H}_5)_3]$ .

The formation<sup>11</sup> of  $\text{Li}[\text{Cd}(\text{C}_6\text{H}_5)_3]$  from  $(\text{C}_6\text{H}_5)_2\text{Cd}$  and  $\text{C}_6\text{H}_5\text{Li}$  belongs to the same reaction type.

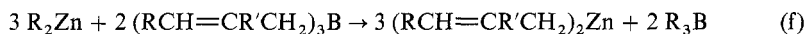
(K.-H. THIELE)

1. H. Lehmkuhl, H. Nehl, *J. Organomet. Chem.*, **221**, 131 (1981).
2. H. D. Visser, C. P. Stodulsk, J. P. Oliver, *J. Organomet. Chem.*, **24**, 563 (1970).
3. K.-H. Thiele, J. Köhler, *J. Prakt. Chem.*, **32**, 54 (1966).
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5. K.-H. Thiele, G. Engelhardt, J. Köhler, M. Arnstedt, *J. Organomet. Chem.*, **9**, 385 (1967).
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9. H. Gilman, L. A. Woods, *J. Am. Chem. Soc.*, **67**, 520 (1945).
10. D. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).
11. G. Wittig, F. J. Meyer, G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951).

### 5.7.3. Silicon-Group-IIB Bonds

These structures include symmetrical alkyls, aryls, fluoroaryls and alkylhydrides of Si bonded<sup>1-4</sup> to Zn, Cd and Hg. The compounds  $(\text{R}_3\text{Si})_2\text{M}$  (where  $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ) are yellow, crystalline, monomeric solids, sensitive to both hydrolysis and atmospheric oxidation. In addition, the unsymmetrical compounds  $\text{R}_3\text{SiMX}$  (where  $\text{X} = \text{anionic ligand}$ ) are isolated either by direct synthesis or, more usually, by the cleavage of one  $\text{Si}-\text{M}$  bond in a symmetrical compound, which is the only method available for certain  $\text{Si}-\text{M}-\text{X}$  compounds.

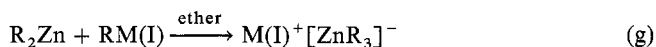
Reactions of simple zinc dialkyls and boron triallyls at RT:



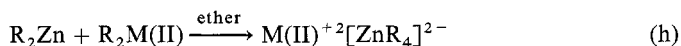
allow the synthesis of zinc diallyls, which cannot be prepared pure by other methods<sup>4,5</sup>. The alkyl-allyl exchange takes place in seconds and resembles an ionic reaction. Using  $\text{Me}_2\text{Zn}$  as starting material, pure allylzincs are obtained, because the volatile  $\text{Me}_3\text{B}$  evaporates completely from the mixture.

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Complex formation of the type:



where  $\text{M}(\text{I}) = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ , and:



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The formation<sup>11</sup> of  $\text{Li}[\text{Cd}(\text{C}_6\text{H}_5)_3]$  from  $(\text{C}_6\text{H}_5)_2\text{Cd}$  and  $\text{C}_6\text{H}_5\text{Li}$  belongs to the same reaction type.

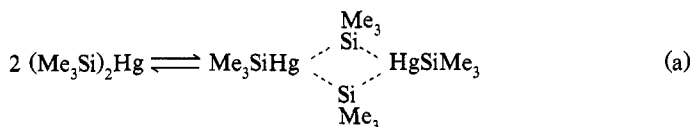
(K.-H. THIELE)

1. H. Lehmkuhl, H. Nehl, *J. Organomet. Chem.*, **221**, 131 (1981).
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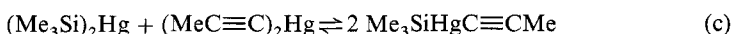
### 5.7.3. Silicon-Group-IIB Bonds

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In this section and in §5.7.4 redistribution reactions are referred to that involve the breaking and making of Si—Hg and Ge—Hg bonds. In their simplest form these are self-exchange reactions that show second-order kinetics with large negative entropies of activation consistent with an electron-deficient transition state, e.g.:



At RT, solutions of  $(\text{Me}_3\text{Si})_2\text{Hg}$  or  $(\text{Me}_3\text{Ge})_2\text{Hg}$  show a single  $^1\text{H}$ -NMR resonance flanked by  $^{199}\text{Hg}$  satellites. As the temperature is raised the satellite signals broaden and finally collapse as the exchange rate becomes rapid on the NMR time scale. Exchange reactions between different silylmercurials and between silylmercurials and mercury dialkyls are elucidated<sup>5</sup> by NMR, e.g.:

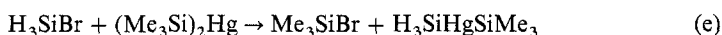


The kinetics of thermal decomposition of  $(\text{Me}_3\text{Si})_2\text{Hg}$  in solution may be interpreted in terms of a simple bimolecular reaction yielding Hg and  $\text{Me}_6\text{Si}_2$  via a Hg(I) intermediate<sup>6</sup>:



The chemistry of mercury(II) is dominated by the stability of two-coordinated compounds but in silylmercury compounds three- and four-coordinated anions,  $[(\text{R}_3\text{Si})_3\text{Hg}]^-$  and  $[(\text{R}_3\text{Si})_4\text{Hg}]^{2-}$  are formed.

Most isolable silylmercury compounds have three organic groups bonded to silicon, but the formation of  $\text{H}_3\text{SiHg}$  derivatives is achieved by:



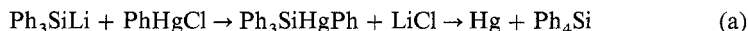
These silyl mercurials are stable over several days at RT, but as solids they react with traces of air or  $\text{H}_2\text{O}$ . Organo(chloro)silylmercurials,  $(\text{R}_n\text{Cl}_{3-n}\text{Si})_2\text{Hg}$  ( $n = 0-2$ ), also are known<sup>7</sup>.

(F. GLOCKLING)

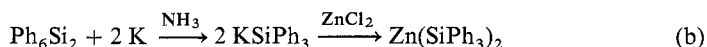
1. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya, *Organomet. Chem. Rev.*, **A**, *3*, 323 (1968); a review.
2. E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, E. Straude, *Angew. Chem., Int. Ed. Engl.*, *2*, 507 (1963); a review.
3. R. F. Cunico, *J. Organomet. Chem.*, *109*, 1 (1974).
4. D. Seyferth, *J. Organomet. Chem.*, *130*, 173 (1977); *143*, 153 (1977); *176*, 137 (1979); *183*, 141 (1979); *203*, 183 (1980); reviews covering Si—Hg and Ge—Hg chemistry for 1975–1979.
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6. C. Eaborn, R. A. Jackson, R. W. Walsingham, *J. Chem. Soc., Perkin Trans. 2*, 366 (1973).
7. C. R. Bettler, J. C. Sandra, G. Urry, *Inorg. Chem.*, *9*, 1060 (1970).

### 5.7.3.1. from Silyl-Alkali-Metal Reagents with Group-IIB Halides and Organohalides.

Treatment of triphenylgermyllithium with phenylmercury(II) chloride gives Hg and tetraphenylsilane<sup>1</sup>, products that can be understood on the basis of the intermediate formation of  $\text{Ph}_3\text{SiHgPh}$ :



However, the earliest method leading to the isolation of organosilyl derivatives of Zn, Cd and Hg makes use of liq  $\text{NH}_3$  as solvent for the formation of  $\text{R}_3\text{Si}$ -alkali-metal complexes. For example, when hexaphenyldisilane is treated with potassium in liq  $\text{NH}_3$  a red-brown solution of solvated  $\text{KSiPh}_3$  is formed and, on addition of anhyd  $\text{ZnCl}_2$ , the color is discharged in an exothermic reaction:

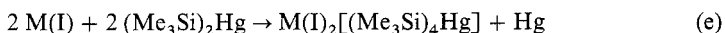


The white silyl-Zn solid precipitates from benzene in 85% yield. It decomposes at  $> 105^\circ\text{C}$  to form Zn. With  $\text{NH}_3$  it forms a complex,  $(\text{NH}_3)_2\text{Zn}(\text{SnPh}_3)_2$ .

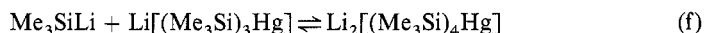
When bright yellow, solid bis(trimethylsilyl)mercury is treated with trimethylsilyllithium in 1,2-dimethoxyethane (DME), color changes occur and either a three- or a four-coordinated anionic silyl-Hg compound may be isolated according to the stoichiometry<sup>2</sup>:



Although in these complexes the cations are solvated, it is possible to desolvate them without decomposition. Similarly, alkali metals react with bis(trimethylsilyl)mercury:

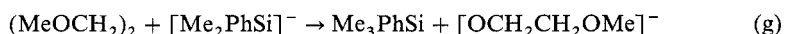


where M(I) is an alkali metal. From NMR studies in DME there is no dissociation of the three-coordinated anion, but in the presence of  $(\text{Me}_3\text{Si})_2\text{Hg}$  rapid transfer of  $\text{Me}_3\text{Si}$  groups between the two Hg sites is observed. Similarly, solutions of  $\text{Li}_2[(\text{Me}_3\text{Si})_4\text{Hg}]$  and  $\text{Li}[(\text{Me}_3\text{Si})_3\text{Hg}]$  undergo rapid exchange of  $\text{Me}_3\text{Si}$  groups:

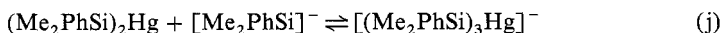
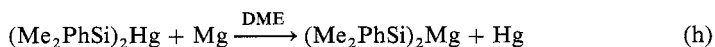


The equilibrium lies to the left at  $20^\circ\text{C}$  (red color) and to the right at low T (green color). The structures of the related silylmercury complexes,  $\text{Li}[(\text{Me}_2\text{PhSi})_3\text{Hg}]$  and  $\text{Li}_2[(\text{Me}_2\text{PhSi})_4\text{Hg}]$ , contain a symmetrical, planar monoanion and a  $\text{T}_d$  dianion.

Magnesium also reacts with  $(\text{Me}_2\text{PhSi})_2\text{Hg}$  in DME to produce deep-red crystals that contain the anion  $[(\text{Me}_2\text{PhSi})_3\text{Hg}]^-$  and the cation,  $[\text{Mg}_4(\text{DME})_6(\text{DME})]^{2+}$ , which results from demethylation of the ether<sup>3</sup>:



The steps in this reaction are:

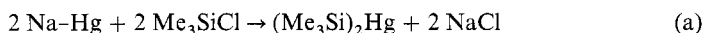




1. M. V. George, G. D. Lichtenwalner, H. Gilman, *J. Am. Chem. Soc.*, **81**, 978, (1959).
2. T. F. Schaaf, J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 4327 (1969).
3. E. A. Sadurski, W. H. Ilsley, R. D. Thomas, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **100**, 7761 (1978).

### 5.7.3.2. from Organohalosilanes with Na or Al Amalgam.

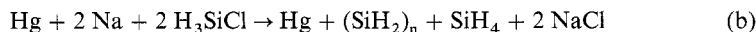
Bis(trimethylsilyl)mercury is prepared by shaking together 1% Na amalgam with either neat  $\text{Me}_3\text{SiCl}$  or its cyclohexane solution. An inert atmosphere is essential, although  $(\text{Me}_3\text{Si})_2\text{Hg}$  is stable to  $\text{H}_2\text{O}$ . The yield is greater if  $\text{Me}_3\text{SiI}$  or  $\text{Me}_3\text{SiBr}$  is used, but the commercial availability of  $\text{Me}_3\text{SiCl}$  and its low cost offset this advantage:



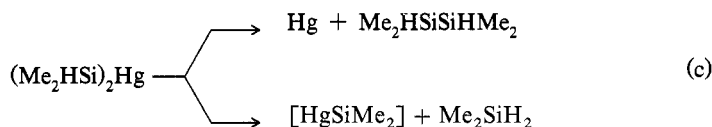
Decantation from xs Hg and NaCl followed by removal of liquid products in vacuo leaves  $(\text{Me}_3\text{Si})_2\text{Hg}$  as highly refracting yellow crystals that may be purified by vacuum sublimation at  $60^\circ\text{C}$ . The crystals are soluble in most organic solvents and melt with decomposition at ca.  $100^\circ\text{C}$  to yield Hg,  $\text{Me}_6\text{Si}_2$  and  $(\text{Me}_3\text{Si})_2\text{Hg}$  which is more stable than  $(\text{Me}_3\text{C})_2\text{Hg}$ .

A more rapid and reliable method for  $(\text{Me}_3\text{Si})_2\text{Hg}$  consists<sup>1</sup> of heating Al, Hg and xs  $\text{Me}_3\text{SiCl}$  in tetrahydrofuran (THF).

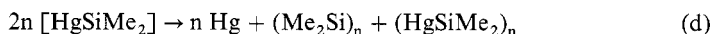
Where hydrogen is also bonded to Si the stability of the silylmercury product is reduced, and with chlorosilanes the formation of  $(\text{H}_3\text{Si})_2\text{Hg}$  can only be inferred from the final products:



Similarly, methylbromosilane only yields decomposition products including methylsilane by reaction with Na-Hg. Dimethylbromosilane reacts with Na-Hg to give  $(\text{Me}_2\text{HSi})_2\text{Hg}$ , which is thermally unstable. Its thermolysis proceeds by two routes, one of which produces dimethylsilylenemercury:



on which there is no structural information; it decomposes partly to a polymer and partly to Hg metal:



The same polymeric silylmercurial can be obtained as a viscous oil, stable to  $60^\circ\text{C}$ , by:



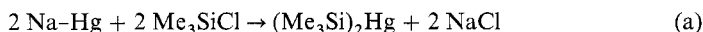
Bis(triphenylsilyl)mercury,  $(\text{Ph}_3\text{Si})_2\text{Hg}$ , is also prepared from Na amalgam and  $\text{Ph}_3\text{SnCl}$  although in liq  $\text{NH}_3$ . Here there is evidence for an intermediate with one Si–Hg bond, viz.,  $\text{Ph}_3\text{SiHgCl}$ . This reaction is less satisfactory because of the facile formation of  $\text{Ph}_3\text{SiNH}_2$  (from  $\text{Ph}_3\text{SiHgCl}$ ) and  $\text{Ph}_6\text{Si}_2$  [by thermal decomposition of  $(\text{Ph}_3\text{Si})_2\text{Hg}$ ].

5.7. Formation of Bonds between Elements of Groups IVB and IIB 343  
 5.7.3. Silicon–Group-IIB Bonds

1. M. V. George, G. D. Lichtenwalner, H. Gilman, *J. Am. Chem. Soc.*, **81**, 978, (1959).
2. T. F. Schaaf, J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 4327 (1969).
3. E. A. Sadurski, W. H. Ilsley, R. D. Thomas, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **100**, 7761 (1978).

**5.7.3.2. from Organohalosilanes with Na or Al Amalgam.**

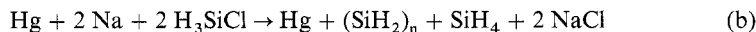
Bis(trimethylsilyl)mercury is prepared by shaking together 1 % Na amalgam with either neat  $\text{Me}_3\text{SiCl}$  or its cyclohexane solution. An inert atmosphere is essential, although  $(\text{Me}_3\text{Si})_2\text{Hg}$  is stable to  $\text{H}_2\text{O}$ . The yield is greater if  $\text{Me}_3\text{SiI}$  or  $\text{Me}_3\text{SiBr}$  is used, but the commercial availability of  $\text{Me}_3\text{SiCl}$  and its low cost offset this advantage:



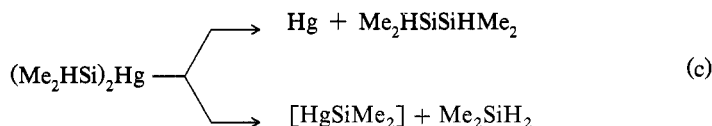
Decantation from xs Hg and NaCl followed by removal of liquid products in vacuo leaves  $(\text{Me}_3\text{Si})_2\text{Hg}$  as highly refracting yellow crystals that may be purified by vacuum sublimation at  $60^\circ\text{C}$ . The crystals are soluble in most organic solvents and melt with decomposition at ca.  $100^\circ\text{C}$  to yield Hg,  $\text{Me}_6\text{Si}_2$  and  $(\text{Me}_3\text{Si})_2\text{Hg}$  which is more stable than  $(\text{Me}_3\text{C})_2\text{Hg}$ .

A more rapid and reliable method for  $(\text{Me}_3\text{Si})_2\text{Hg}$  consists<sup>1</sup> of heating Al, Hg and xs  $\text{Me}_3\text{SiCl}$  in tetrahydrofuran (THF).

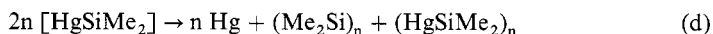
Where hydrogen is also bonded to Si the stability of the silylmercury product is reduced, and with chlorosilanes the formation of  $(\text{H}_3\text{Si})_2\text{Hg}$  can only be inferred from the final products:



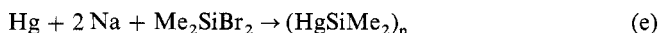
Similarly, methylbromosilane only yields decomposition products including methylsilane by reaction with Na–Hg. Dimethylbromosilane reacts with Na–Hg to give  $(\text{Me}_2\text{HSi})_2\text{Hg}$ , which is thermally unstable. Its thermolysis proceeds by two routes, one of which produces dimethylsilylenemercury:



on which there is no structural information; it decomposes partly to a polymer and partly to Hg metal:

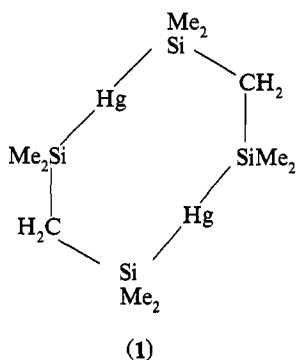


The same polymeric silylmercurial can be obtained as a viscous oil, stable to  $60^\circ\text{C}$ , by:



Bis(triphenylsilyl)mercury,  $(\text{Ph}_3\text{Si})_2\text{Hg}$ , is also prepared from Na amalgam and  $\text{Ph}_3\text{SnCl}$  although in liq  $\text{NH}_3$ . Here there is evidence for an intermediate with one Si–Hg bond, viz.,  $\text{Ph}_3\text{SiHgCl}$ . This reaction is less satisfactory because of the facile formation of  $\text{Ph}_3\text{SiNH}_2$  (from  $\text{Ph}_3\text{SiHgCl}$ ) and  $\text{Ph}_6\text{Si}_2$  [by thermal decomposition of  $(\text{Ph}_3\text{Si})_2\text{Hg}$ ].

Sodium amalgam acts on  $(\text{Me}_2\text{ClSi})_2\text{CH}_2$  to produce<sup>1,2</sup> greenish-yellow crystals, sublimable in vacuo at  $100^\circ\text{C}$  without decomposition, comprised of eight-membered rings (I) with linear Si—Hg—Si bonds:

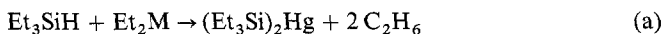


(F. GLOCKLING)

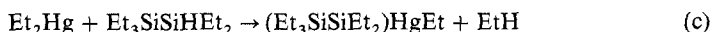
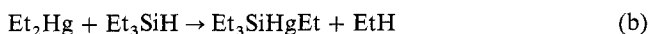
1. L. Rösch, W. Erb, *Chem. Ber.*, **112**, 394 (1979).
2. M. A. Albright, T. F. Schaaf, W. M. Butler, A. K. Howard, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **97**, 6261 (1975).
3. C. R. Bettler, G. Urry, *Inorg. Chem.*, **9**, 2372 (1970).

### 5.7.3.3. from Organosilicon Hydrides with Zn, Cd and Hg Dialkyls.

Neat triethylsilane reacts<sup>1–3</sup> with neat  $\text{Et}_2\text{Zn}$ ,  $\text{Et}_2\text{Cd}$  and  $\text{Et}_2\text{Hg}$ :

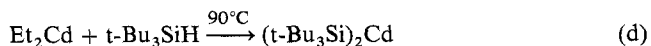


in an inert atmosphere or vacuum with mild heating. The Si—M bonds are formed stepwise, but it is not always possible to isolate the intermediate  $\text{Et}_3\text{SiMEt}$ :



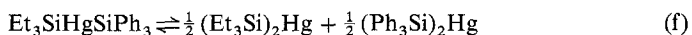
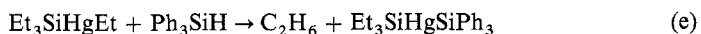
Dibenzylmercury is sufficiently reactive to convert triphenylsilane into toluene and  $(\text{Ph}_3\text{Si})_2\text{Hg}$ .

The reaction may be applied widely and is not susceptible to steric inhibition, e.g.:



Yields are  $> 50\%$ . In the reaction between  $\text{Et}_3\text{SiH}$  and  $\text{Et}_2\text{Hg}$  the byproduct,  $\text{Et}_3\text{SiHgSiEt}_2\text{SiEt}_3$ , is isolated.

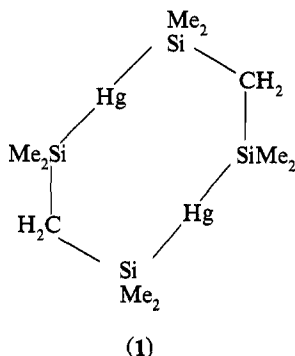
Unsymmetrical silylmercurials can be cleaved with formation of a second Si—Hg bond; these reactions are followed by a disproportionation step:



The cleavages are not selective, and in the above example  $\text{Ph}_4\text{SiHgEt}$  is formed also.

344 5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.3. Silicon-Group-IIB Bonds

Sodium amalgam acts on  $(\text{Me}_2\text{ClSi})_2\text{CH}_2$  to produce<sup>1,2</sup> greenish-yellow crystals, sublimable in vacuo at  $100^\circ\text{C}$  without decomposition, comprised of eight-membered rings (I) with linear Si—Hg—Si bonds:

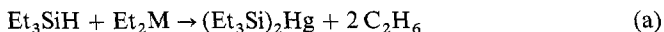


(F. GLOCKLING)

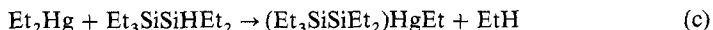
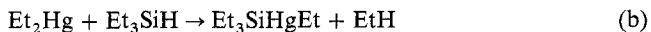
1. L. Rösch, W. Erb, *Chem. Ber.*, **112**, 394 (1979).
2. M. A. Albright, T. F. Schaaf, W. M. Butler, A. K. Howard, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **97**, 6261 (1975).
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**5.7.3.3. from Organosilicon Hydrides with Zn, Cd and Hg Dialkyls.**

Neat triethylsilane reacts<sup>1-3</sup> with neat  $\text{Et}_2\text{Zn}$ ,  $\text{Et}_2\text{Cd}$  and  $\text{Et}_2\text{Hg}$ :

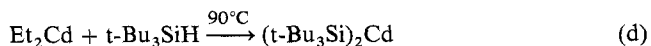


in an inert atmosphere or vacuum with mild heating. The Si—M bonds are formed stepwise, but it is not always possible to isolate the intermediate  $\text{Et}_3\text{SiMEt}$ :



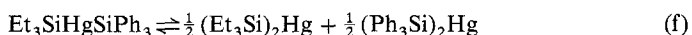
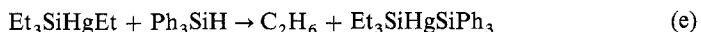
Dibenzylmercury is sufficiently reactive to convert triphenylsilane into toluene and  $(\text{Ph}_3\text{Si})_2\text{Hg}$ .

The reaction may be applied widely and is not susceptible to steric inhibition, e.g.:



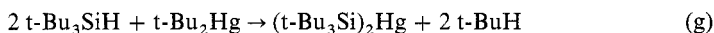
Yields are  $> 50\%$ . In the reaction between  $\text{Et}_3\text{SiH}$  and  $\text{Et}_2\text{Hg}$  the byproduct,  $\text{Et}_3\text{SiHgSiEt}_3$ , is isolated.

Unsymmetrical silylmercurials can be cleaved with formation of a second Si—Hg bond; these reactions are followed by a disproportionation step:



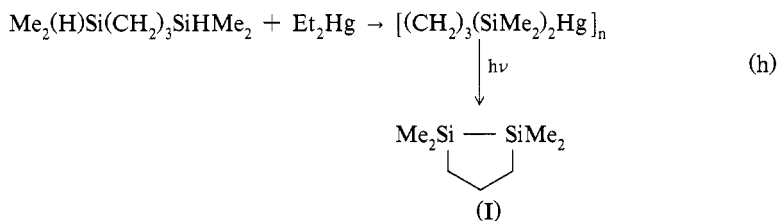
The cleavages are not selective, and in the above example  $\text{Ph}_4\text{SiHgEt}$  is formed also.

Unsymmetrical silylmercurials are more resistant to symmetrization than dialkylmercurials,  $RR'Hg$ . The low steric factor in these silane substitution reactions is apparent in the reaction:

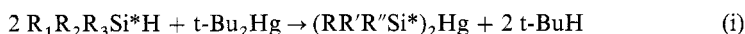


which takes place at  $70^\circ\text{C}$  in 70% yield<sup>4</sup>.

The silane,  $\text{Me}_2(\text{H})\text{Si}(\text{CH}_2)_3\text{SiHMe}_2$ , reacts with  $\text{Et}_2\text{Hg}$  to give a polymeric  $\text{Si—Hg}$  derivative, which on irradiation breaks down into Hg and the heterocycle (I)<sup>5</sup>:

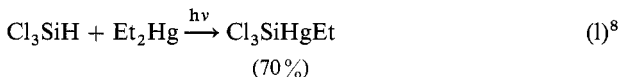
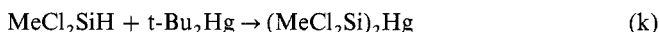
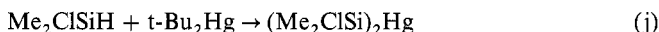


Optically active silylmercurials are obtained by<sup>6</sup>:

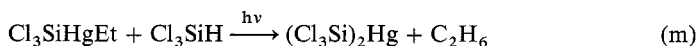


where R, R', R'' = Me, Ph,  $1\text{-C}_{10}\text{H}_7$ .

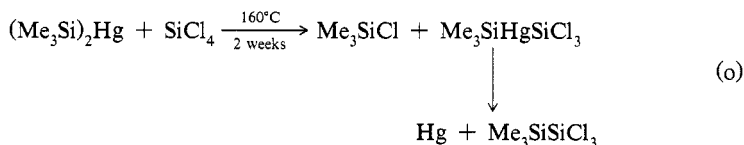
Most bis-silylmercurials are of the organo- $(\text{R}_3\text{Si})_2\text{Hg}$  type, but compounds with one to three  $\text{Si—Cl}$  bonds are known. They are thermally stable but sensitive to photodecomposition<sup>7</sup>:



Increased chlorination at Si reduces the rate of self-exchange (scrambling) of silyl groups. Pure  $\text{Cl}_3\text{SiHgEt}$  melts with decomposition at ca.  $80^\circ\text{C}$ ; it may be sublimed in vacuo, and cleavage of the  $\text{Hg—Et}$  bond by  $\text{HBr}$  or  $\text{HI}$  provides a route to  $\text{Cl}_3\text{SiHgX}$ . The bis-compound,  $(\text{Cl}_3\text{Si})_2\text{Hg}$ , is obtained from:



It decomposes at  $> 250^\circ\text{C}$  to Hg and  $\text{Si}_2\text{Cl}_6$ . The cleavage of bis(trimethylsilyl)methylmercury by  $\text{SiCl}_4$  proceeds via an  $\text{Hg—SiCl}_3$  intermediate<sup>9</sup>, whereas UV irradiation of this mercurial in the presence of  $\text{SiHCl}_3$  gives  $(\text{Cl}_3\text{Si})_2\text{Hg}$ :

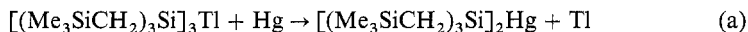


(F. GLOCKLING)

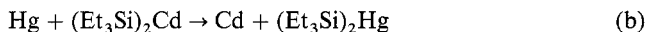
1. N. S. Vyazankin, V. T. Bychkov, I. A. Vostokov, *J. Gen. Chem. USSR (Engl. Transl.)*, **38**, 1297 (1968).
2. N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, *Dokl. Chem. (Engl. Transl.)*, **155**, 302 (1964).
3. N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, T. G. Gurikova, *Dokl. Chem. (Engl. Transl.)*, **155**, 360 (1964).
4. H. Muller, L. Rösch, *J. Organomet. Chem.*, **133**, 1 (1977).
5. R. J. P. Corriu, G. F. Lanneau, D. Leclercq, D. Samate, *J. Organomet. Chem.*, **144**, 155 (1978).
6. C. Eaborn, R. A. Jackson, D. J. Tune, D. R. M. Walton, *J. Organomet. Chem.*, **63**, 85 (1973).
7. T. F. Schaaf, R. R. Kao, J. P. Oliver, *Inorg. Chem.*, **14**, 2288 (1975).
8. G. A. Marino, A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **5**, 621 (1969).
9. F. Glockling, J. J. Sweeney, *J. Chem. Res., (S)*, **35**; (*M*), 615 (1977).

#### 5.7.3.4. from Silylcadmiums and -Thalliums with Hg Metal.

These reactions are of little preparative value, but do relate to equilibria and mechanistic studies<sup>1</sup>:



Bis(trimethylsilyl)cadmium and -thallium also react with Hg. The reactions are fast at 50°C:



(F. GLOCKLING)

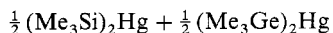
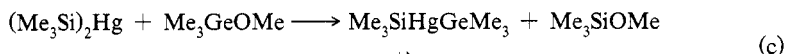
1. G. S. Kalinina, E. A. Shchupak, N. S. Vyazankin, G. A. Razuvaev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **25**, 1289 (1976).

#### 5.7.3.5. from Redistribution and Related Reactions.

Redistribution of alkyl groups between Hg dialkyls is slow at RT; by contrast, the more weakly bonded silyl- and germylmercurials exchange rapidly, yielding an equilibrium concentration of the unsymmetrical compound<sup>1,2</sup>:

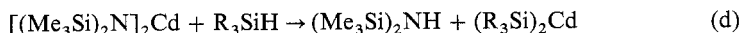


When  $(\text{Me}_3\text{Si})_2\text{Hg}$  is cleaved by  $\text{Me}_3\text{GeOMe}$  or  $\text{Me}_3\text{SnOMe}$  the unsymmetrical compounds are formed, and these slowly equilibrate with the symmetrical species, e.g.:



With  $\text{HgCl}_2$ ,  $(\text{Et}_3\text{Si})_2\text{Cd}$  reacts exothermically to give Hg metal and  $\text{Me}_3\text{SiCl}$ , products suggestive of  $\text{Si}-\text{Hg}$  intermediates.

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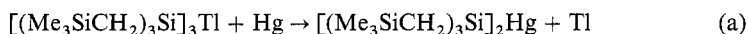


346      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.3. Silicon-Group-IIB Bonds

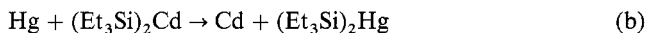
1. N. S. Vyazankin, V. T. Bychkov, I. A. Vostokov, *J. Gen. Chem. USSR (Engl. Transl.)*, **38**, 1297 (1968).
2. N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, *Dokl. Chem. (Engl. Transl.)*, **155**, 302 (1964).
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9. F. Glockling, J. J. Sweeney, *J. Chem. Res., (S)*, **35**; (*M*), 615 (1977).

**5.7.3.4. from Silylcadmiums and -Thalliums with Hg Metal.**

These reactions are of little preparative value, but do relate to equilibria and mechanistic studies<sup>1</sup>:



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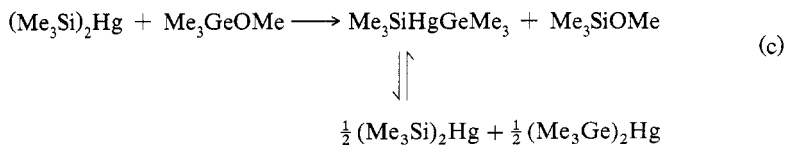
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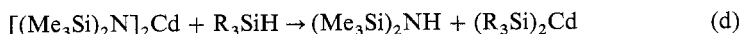


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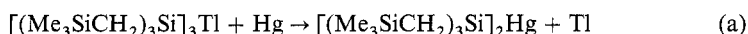


346      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
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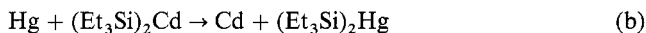
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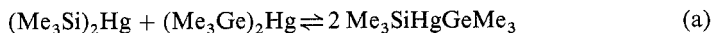


(F. GLOCKLING)

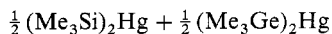
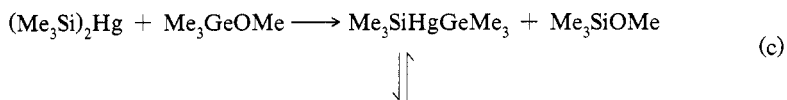
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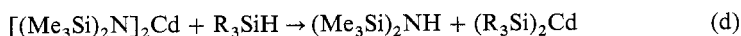


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Silyl–Cd compounds also are made from the silane and metal amide:





Amidomercury compounds behave similarly:



Anionic silylmercurials (see §5.7.3.1) are also formed by the reaction of  $(\text{Et}_3\text{Si})_2\text{Hg}$  with KCN in the presence of crown ethers, the products<sup>2</sup> being  $\text{Et}_3\text{SiCN}$  and  $\text{K}_2[\text{Hg}(\text{SiEt}_3)_4]$ .

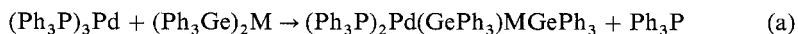
(F GLOCKLING)

1. S. W. Bennett, H. J. Clase, C. Eaborn, R. A. Jackson, *J. Organomet. Chem.*, **23**, 403 (1970).
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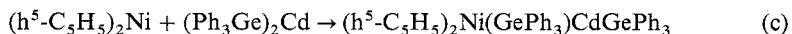
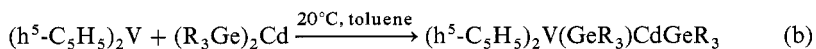
#### 5.7.4. Ge—Group-IIB Bonds

The structures in this section are similar to those considered in §5.7.3. Germanium(IV) forms covalent bonds to Zn, Cd and Hg, yielding monomers<sup>1-7</sup>. Alkyl, aryl and perfluorophenyl groups also bond to Ge, and similar compounds are formed by Zn, Cd and Hg, although germylmercurials, are best known. Both symmetrical [e.g.,  $(\text{Me}_3\text{Ge})_2\text{Hg}$ ] and unsymmetrical e.g.,  $\text{R}_3\text{GeMX}$ , compounds are known. With Zn and Cd other neutral ligands can bond, raising the coordination number to three or four. Most of the germylmercurials are two-coordinated, but there are examples of anions  $[(\text{R}_3\text{Ge})_3\text{Hg}]^-$  and  $[(\text{R}_3\text{Ge})_4\text{Hg}]^{2-}$ ; e.g., praseodymium displaces Hg from  $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg}$  to form<sup>8</sup> the complex  $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Pr}^+ + 2 [(\text{C}_6\text{F}_5)_3\text{Ge}]_3\text{Hg}^-$ .

Although many unsymmetrical,  $\text{R}_3\text{GeMX}$ , compounds can be made by the methods discussed in the following sections, others can be obtained only by cleavage of a preformed Ge—M bond, e.g.:



where M = Cd, Hg;



All Ge—M compounds are sensitive to hydrolysis and oxidation, although the decomposition rates do not pose serious experimental difficulties.

Although almost all Ge—M compounds have three organic ligands bonded to Ge, structurally simpler  $\text{H}_3\text{Ge—Hg}$  compounds can be isolated:



They are less sensitive to air and  $\text{H}_2\text{O}$  than the silyl analogues, but in solution are less thermally stable<sup>9</sup>. Chlorogermylmercurials, such as  $(\text{Cl}_3\text{Ge})_2\text{Hg}$ , are known also.

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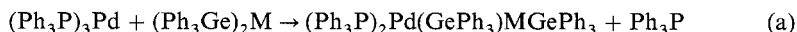
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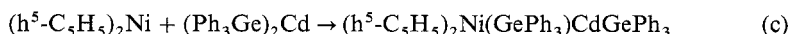
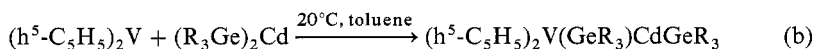
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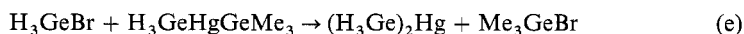


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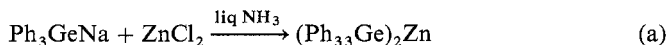
Germylmercurials and related compounds can be separated chromatographically<sup>10</sup> in ether–hexane on Silochrom C-80.

(F. GLOCKLING)

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2. B. C. Pant, *J. Organomet. Chem.*, **48** 125 (1973); **89**, 1 (1975); **119**, 149 (1976).
3. D. A. Armitage, in *Organometallic Chemistry*, Vols. 1–8, *Specialist Periodical Reports*, The Royal Society of Chemistry, London, (1971–1978)
4. F. Glockling, *Organogermanium Chemistry*, Academic Press, New York 1969.
5. M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley, New York, 1971.
6. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya, *Z. Chem.*, **11**, 53 (1971).
7. J. D. Cotton, *Organomet. Chem.*, **1**, 194 (1972).
8. G. A. Razuvaev, L. N. Bochkarev, G. S. Kalinina, M. N. Bochkarev, *Inorg. Chim. Acta*, **24**, L40 (1977).
9. S. Craddock, E. A. V. Ebsworth, N. S. Hosmane, K. M. Mackay, *Angew. Chem., Int. Ed. Engl.*, **14**, 167 (1975).
10. M. N. Bochkarev, G. N. Bortnikov, N. P. Makarenko, L. P. Maiorova, *J. Chromatogr.*, **170**, 53 (1979).

#### 5.7.4.1. from Germyl–Alkali-Metal Reagents with Group-IIB Halides and Organohalides.

Organogermyl–alkali-metal reagents are powerful nucleophiles and can establish bonds with Zn, Cd and Hg, e.g., to form a Ge—Zn compound<sup>1,2</sup>:



The Zn product is highly reactive and is more readily isolated as the four-coordinated complex,  $(\text{Ph}_3\text{Ge})_2\text{Zn} \cdot 2 \text{ THF}$  where THF is tetrahydrofuran.

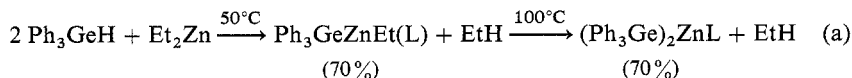
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1. N. S. Vyazankin, G. Razuvaev, V. T. Bychkov, V. L. Zvezdin, *Bull. Acad. Sci. USSR, Div. Chem. Soc.*, 533 (1966).
2. E. Amberger, W. Stoeger, H. R. Grossich, *Angew. Chem., Int. Ed. Engl.*, **5**, 522 (1966).

#### 5.7.4.2. from Organogermanium Hydrides with Zn, Cd and Hg Dialkyls.

This reaction is most successful with Hg and least with Zn, reflecting the relative stabilities of the metal–Ge bonds.

Triethylgermane and  $\text{Et}_2\text{Zn}$  react as neat liquids only at elevated T; by 150°C complex radical processes occur, giving products including Zn metal, ethane and  $\text{Et}_4\text{Ge}$ . In addition a yellow, nonvolatile but soluble product is formed that has the structure  $\text{Et}_3\text{GeZn}(\text{GeEt}_2)_n\text{ZnGeEt}_3$ . By contrast, triphenylgermane reacts with Zn dialkyls in ethers to give either mono- or disubstitution products, stabilized by an electron-pair donor:



where L =  $(\text{MeOCH}_2\text{CH}_2)_2\text{O}$  (diglyme).

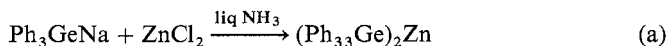
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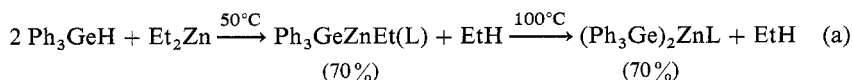
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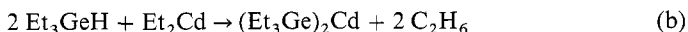


where L =  $(\text{MeOCH}_2\text{CH}_2)_2\text{O}$  (diglyme).

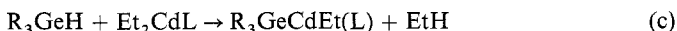
(F. GLOCKLING)

- where  $L = (\text{MeOCH}_2\text{CH}_2)_2\text{O}$  (diglyme).

Diethylcadmium reacts with triethylgermane under milder conditions, and, provided air and H<sub>2</sub>O are excluded, the neat liquids yield (Et<sub>3</sub>Ge)<sub>2</sub>Cd as a solid, stable at RT but completely decomposed after 7 h at 125°C:

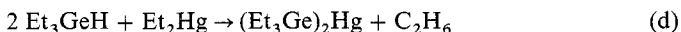


However, in the presence of an electron-pair donor such as diglyme, mono-substituted compounds are stable:



where L = diglyme or hexamethylphosphoramide (HMPA).

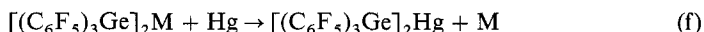
The corresponding Et<sub>2</sub>Hg reaction proceeds in high yield when the two compounds are heated together in an inert atmosphere:



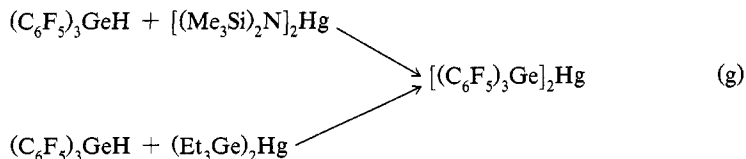
By varying T and the reactant ratio the unsymmetrical Et<sub>3</sub>GeHgEt as well as the symmetrical product can form. These reactions can be selective; e.g., Et<sub>3</sub>SiHgEt and Et<sub>3</sub>GeH react by cleavage of the Hg—Et bond:



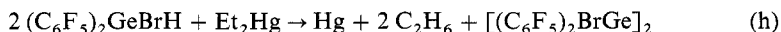
Tris(pentafluorophenyl)germane with Et<sub>2</sub>M (where M = Zn, Cd or Hg) produces [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>M derivatives<sup>1</sup>. The Zn compound is formed over 1 h at 60–100°C in 70% yield and without the complications of polymer formation encountered in the corresponding reaction with Et<sub>3</sub>GeH. It forms air-sensitive crystals, soluble in benzene and toluene, but when crystallized from ether it separates as the solvate, [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Zn·2 OEt<sub>2</sub>, from which the ether may be removed by heating in vacuo. The Cd analogue, [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Cd, also forms crystalline complexes with many monodentate ligands, e.g., [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Cd(PPh<sub>3</sub>)<sub>2</sub>, although not with ether. The Hg compound, [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Hg, which may be prepared either from the germane or by metal exchange:



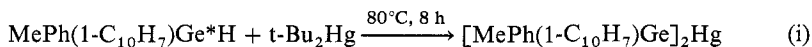
where M = Zn or Cd, is the most thermally stable, mp 228–230°C. The reaction between (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeH and Et<sub>2</sub>Hg can be controlled to give (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeHgEt in 40% yield. The equilibria between (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeH and other germylmercurials or Hg amides favor the formation the perfluorophenylgermyl compounds, e.g.:



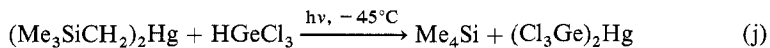
Organogermanium hydrides, e.g., (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>GeBrH, also react with Et<sub>2</sub>Hg, and the presence of a Ge—Hg primary product may be inferred from the materials isolated:



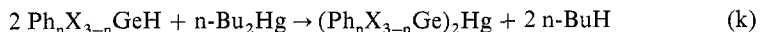
Syntheses of germylmercurials can start with a chiral germane. In both the formation of the Ge—Hg bond and the subsequent cleavage reactions the original configuration is retained, e.g.:



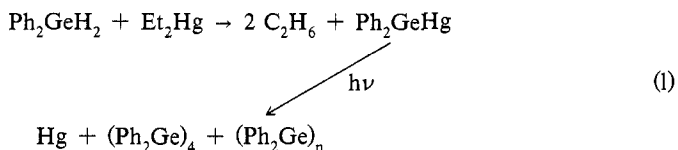
Bis(trichlorogermyl)mercury is prepared by exchange:



If equimolar ratios of reactants are used, the mixed product  $\text{Me}_3\text{SiCH}_2\text{HgGeCl}_3$  may be isolated<sup>2</sup>. Mixed phenylhalogermylmercurials are obtained similarly, e.g.:

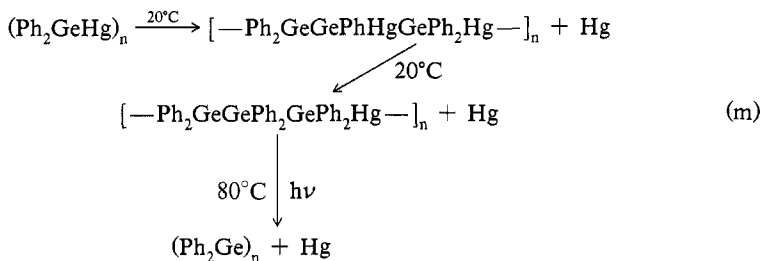


Organogermanium dihydrides and trihydrides react with organomercurials<sup>2</sup>; e.g.,  $\text{Ph}_2\text{GeH}_2$  and  $\text{Et}_2\text{Hg}$  yield ethane and a polymeric Hg—Ge compound that on photolysis or refluxing in benzene decomposes to Hg metal and both cyclic and linear diphenyl-germanes:

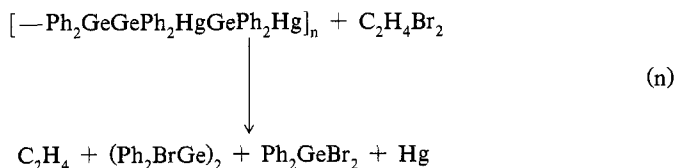


For  $(\text{C}_6\text{F}_5)_2\text{GeH}_2$ , reaction with  $\text{Et}_2\text{Hg}$  is exothermic, and only unidentified insoluble (polymeric) products separate. Similarly,  $(\text{C}_6\text{F}_5)\text{GeH}_3$  and  $\text{Et}_2\text{Hg}$  give  $\text{C}_2\text{H}_6$ , Hg metal and a red, polymeric solid.

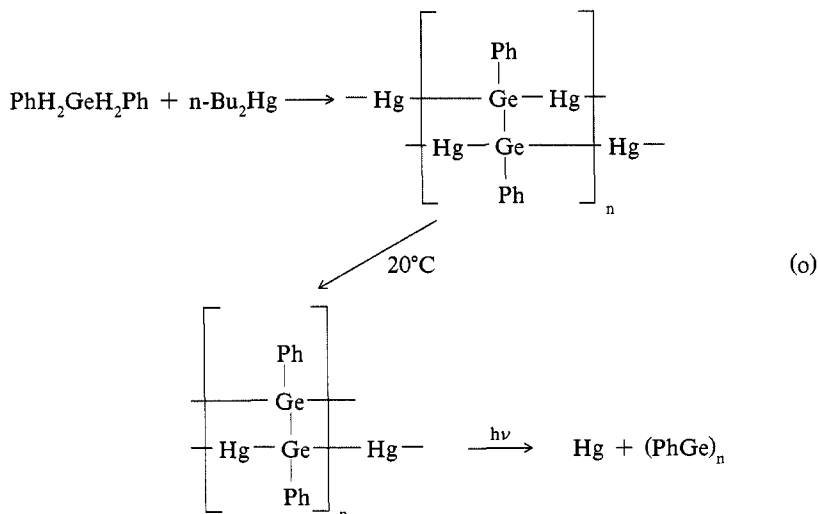
Di- and trihydrides of Ge and  $\text{n-Bu}_2\text{Hg}$  eliminate Hg metal stepwise from the initially formed polymer:



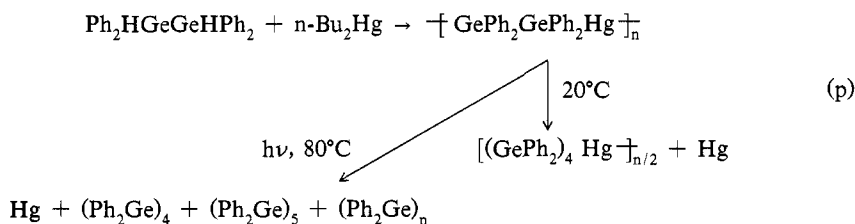
Evidence for these Ge—Ge—Hg-bonded intermediates comes from reacting the mixed products with ethylene dibromide when the Ge—Hg bonds are cleaved quantitatively, e.g.:



Similar stepwise elimination of Hg is observed from the polymer derived from  $(\text{PhH}_2\text{Ge})_2$ , i.e.,  $(\text{Ph}_2\text{Ge}_2\text{Hg}_3)_n$ :



The digermene  $(\text{Ph}_2\text{HGe})_2$  also yields a polymeric germylmercurial with  $n\text{-Bu}_2\text{Hg}$  and, as in the earlier examples, elimination of Hg is observed as a two-stage process:



These polymeric germylmercurials decompose to generate<sup>4,5</sup> germyl radicals,  $[\text{R}_3\text{Ge}]^\cdot$ ; germynes,  $\text{R}_2\text{Ge}$ ; and germynes,  $\text{RGe}$ .

(F. GLOCKLING)

1. M. N. Bochkarev, L. P. Maiorova, S. P. Korneva, L. N. Bocharov, N. S. Vyazankin, *J. Organomet. Chem.*, **73**, 229 (1974).
2. C. R. Bettler, J. C. Sendra, G. Urry, *Inorg. Chem.*, **9**, 1060 (1970).
3. W. P. Neumann, K. Kühlein, *Justus Liebigs Ann. Chem.*, **683**, 1 (1965).
4. P. Rivière, J. Satgé, D. Soula, *C. R. Hebd. Seances Acad. Sci. C*, **277**, 695 (1973).
5. P. Rivière, A. Castel, J. Satgé, *J. Organomet. Chem.*, **212**, 351 (1981).

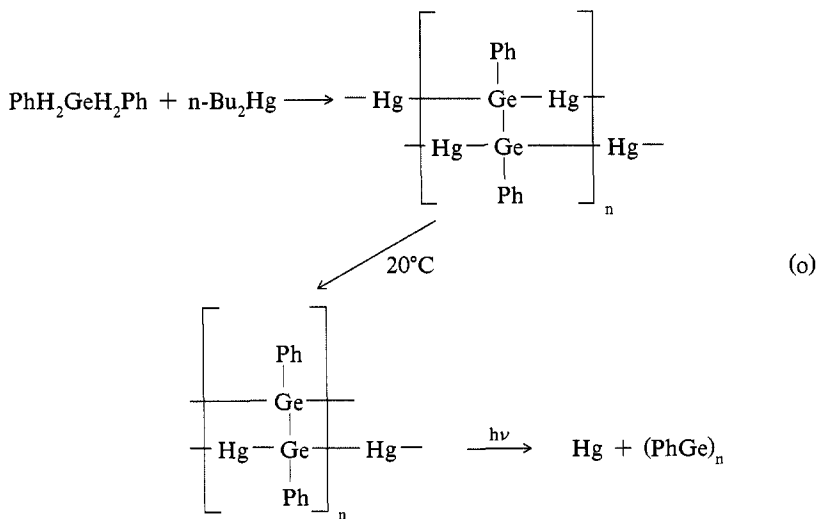
#### 5.7.4.3. from Organohalogermanes with Na Amalgam.

This reaction is simpler and safer than other methods in that organohalogermanes are available, stable compounds, and the volatile, toxic Hg dialkyls are avoided; however, organogermylmercurials are toxic and have an offensive smell.

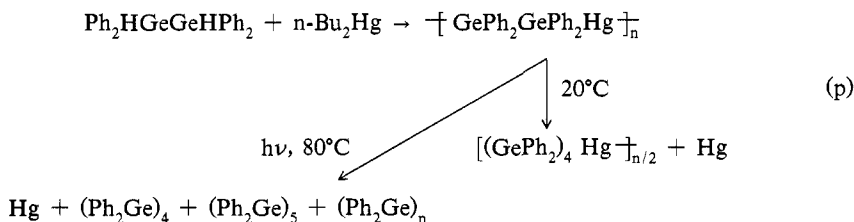


5.7. Formation of Bonds between Elements of Groups IVB and IIB 351  
 5.7.4. Ge–Group-IIB Bonds

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The digermane  $(\text{Ph}_2\text{HGe})_2$  also yields a polymeric germylmercurial with  $n\text{-Bu}_2\text{Hg}$  and, as in the earlier examples, elimination of Hg is observed as a two-stage process:



These polymeric germylmercurials decompose to generate<sup>4,5</sup> germyl radicals,  $[\text{R}_3\text{Ge}]^\cdot$ ; germynes,  $\text{R}_2\text{Ge}$ ; and germynes,  $\text{RGe}$ .

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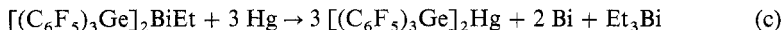
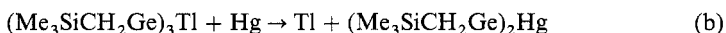
A large xs of Na amalgam (1–2%) reacts in dry cyclohexane either in N<sub>2</sub> or in vacuum<sup>1</sup> after 1–10 days of shaking. The first sign of reaction is the appearance of a pale-yellow color when the amalgam settles, and the color deepens progressively as the (R<sub>3</sub>Ge)<sub>2</sub>Hg concentration increases. Irradiation with strong visible or UV light is not beneficial. Bis(trimethylgermyl)mercury is obtained in 30–40% yield. The workup involves decanting through a fine sinter in an inert atmosphere, evaporating the solvent, and then subliming traces of Hg metal onto a cold finger before subliming (Me<sub>3</sub>Ge)<sub>2</sub>Hg, which forms highly refracting yellow crystals that are stable at ≤ 140°C. Even at 160°C it is only 10% decomposed after 19 h.

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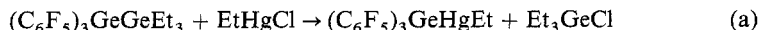
These reactions, which are slow at RT, are useful for determining mechanism and relative reactivity, but are of limited synthetic utility.

(F. GLOCKLING)

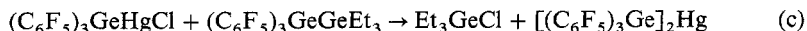
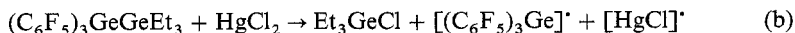
1. G. S. Kalinina, E. A. Shchupak, N. S. Vyazankin, G. A. Razuvaev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 25, 1289 (1976).
2. O. A. Kruglaya, L. I. Belousova, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, 48, 1314 (1978).
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#### 5.7.4.5. from Digermanes with Hg(II) Compounds.

Digermanes with fluorophenyl substituents react with HgCl<sub>2</sub> and EtHgCl to cleave<sup>1</sup> the Ge—Ge bond at RT in tetrahydrofuran (THF), e.g.:



This digermane is readily hydrolyzed. The reactions with HgCl<sub>2</sub> and EtHgCl proceed by an initial one-electron transfer, followed by radical dimerization:



352      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.4. Ge-Group-IIB Bonds

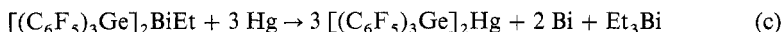
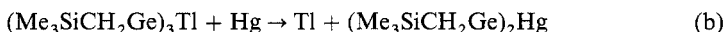
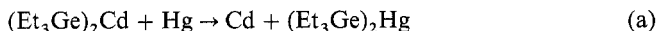
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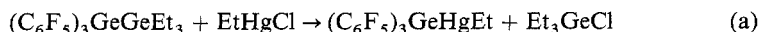
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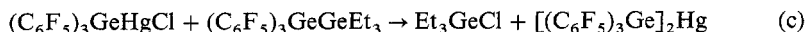
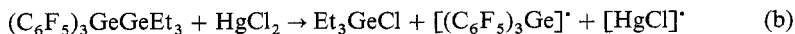
1. G. S. Kalinina, E. A. Shchupak, N. S. Vyazankin, G. A. Razuvaev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **25**, 1289 (1976).
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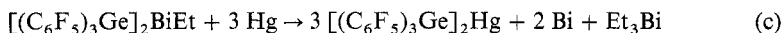
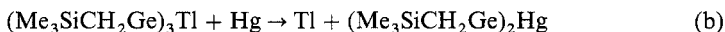
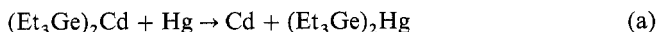
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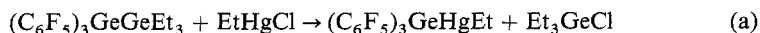
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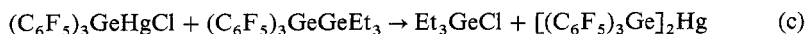
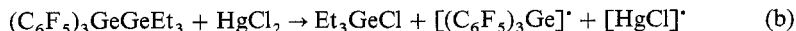
1. G. S. Kalinina, E. A. Shchupak, N. S. Vyazankin, G. A. Razuvaev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **25**, 1289 (1976).
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This digermane is readily hydrolyzed. The reactions with HgCl<sub>2</sub> and EtHgCl proceed by an initial one-electron transfer, followed by radical dimerization:



Neither  $\text{ZnCl}_2$  nor  $\text{CdCl}_2$  is reactive toward the digermane under these conditions, but  $\text{EtHgCl}$  also reacts with the symmetrical fluorophenyldigermane:



(F. GLOCKLING)

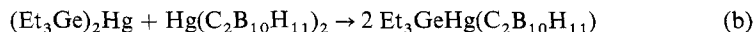
1. M. N. Bochkarev, N. S. Vyazankin, L. N. Bochkarev, G. A. Razuvaev, *J. Organomet. Chem.*, **110**, 149 (1976).

#### 5.7.4.6. from Germyl–Group-IIB Compounds by Redistribution.

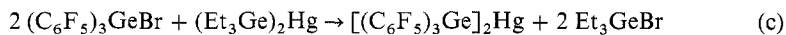
Redistribution of  $(\text{R}_3\text{Ge})_2\text{M}$  with  $\text{MX}_2$  to cleave one  $\text{Ge}—\text{M}$  bond and form another<sup>1,2</sup> is the most satisfactory route to halide derivatives:



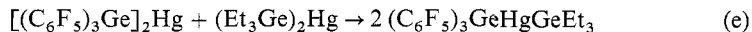
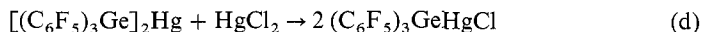
Redistribution forms organogermyl carboranes, e.g.:



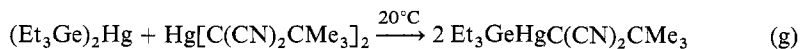
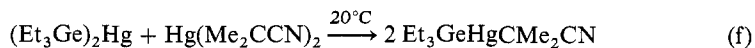
A further variation is provided by exchange, e.g.:



which takes place in benzene in 75 % yield with UV irradiation. Other fluorophenylgermylmercurials also exchange under UV irradiation, e.g.:



Germylmercury–organomercury exchange reactions proceed in high yield under mild conditions, e.g.:



The equilibrium position varies according to the groups bonded to Hg; e.g., in:



the equilibrium lies to the left.

(F. GLOCKLING)

1. M. N. Bochkarev, L. P. Maiorova, N. S. Vyazankin, *J. Organomet. Chem.*, **55**, 89 (1973).
2. T. N. Mitchell, *J. Organomet. Chem.*, **71**, 27 (1974).

5.7. Formation of Bonds between Elements of Groups IVB and IIB 353  
 5.7.4. Ge-Group-IIB Bonds

Neither  $\text{ZnCl}_2$  nor  $\text{CdCl}_2$  is reactive toward the digermene under these conditions, but  $\text{EtHgCl}$  also reacts with the symmetrical fluorophenyldigermene:



(F. GLOCKLING)

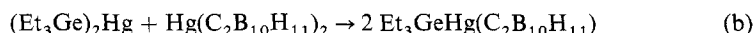
1. M. N. Bochkarev, N. S. Vyazankin, L. N. Bochkarev, G. A. Razuvaev, *J. Organomet. Chem.*, **110**, 149 (1976).

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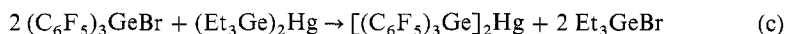
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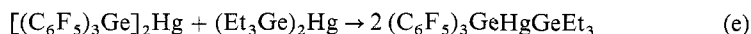
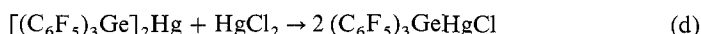
Redistribution forms organogermyl carboranes, e.g.:



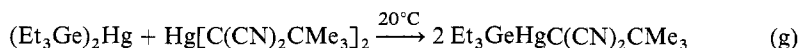
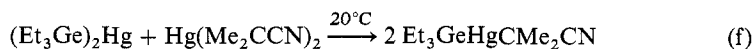
A further variation is provided by exchange, e.g.:



which takes place in benzene in 75% yield with UV irradiation. Other fluorophenylgermylmercurials also exchange under UV irradiation, e.g.:



Germylmercury-organomercury exchange reactions proceed in high yield under mild conditions, e.g.:



The equilibrium position varies according to the groups bonded to Hg; e.g., in:



the equilibrium lies to the left.

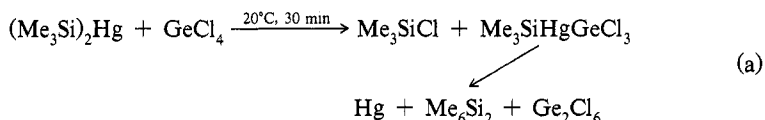
(F. GLOCKLING)

1. M. N. Bochkarev, L. P. Maiorova, N. S. Vyazankin, *J. Organomet. Chem.*, **55**, 89 (1973).
2. T. N. Mitchell, *J. Organomet. Chem.*, **71**, 27 (1974).

354 5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.4. Ge—Group-IIB Bonds

**5.7.4.7. from Silyl- or Germylmercurials and Ge(IV) Halides.**

The only  $\text{GeCl}_4$  reaction under this heading is<sup>1</sup>:



Germyl bromide reacts with bis(trimethylgermyl)mercury to exchange either one or both  $\text{Me}_3\text{Ge}$  groups<sup>2</sup>:

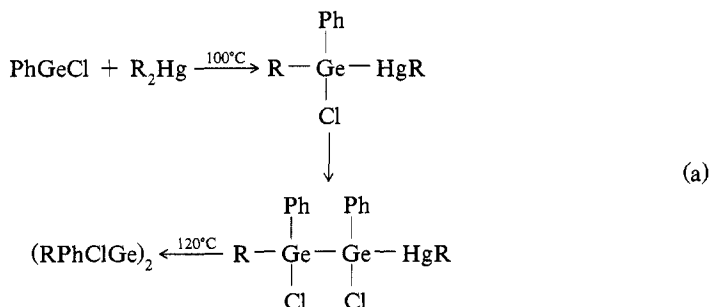


(F. GLOCKLING)

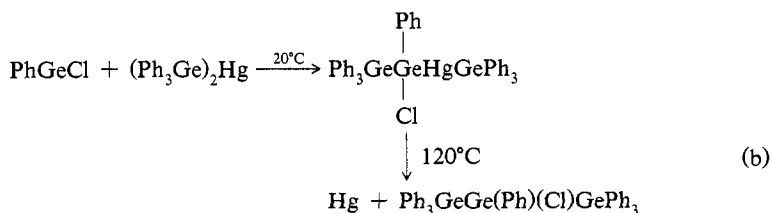
1. F. Glockling, J. J. Sweeney, *J. Chem. Res.*, (S), 35; (M) 615 (1977).
2. S. Cradock, E. A. V. Ebsworth, N. S. Hosmane, K. M. Mackay, *Angew. Chem., Int. Ed. Engl.*, 14, 167 (1975).

**5.7.4.8. by Insertion of Germylenes into Hg—C or Hg—Ge Bonds.**

Germylenes (e.g.,  $\text{GeF}_2$ ,  $\text{PhGeCl}$ ,  $\text{R}_2\text{Ge}$ ) insert into both  $\text{Hg—C}$  and  $\text{Ge—Hg}$  bonds, the reactivity depending on the electrophilicity of the germylene ( $\text{GeX}_2 > \text{RGeX} > \text{R}_2\text{Ge}$ ), e.g.:



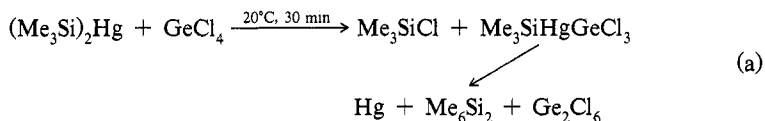
With bis(triphenylgermyl)mercury this reaction takes place at RT:



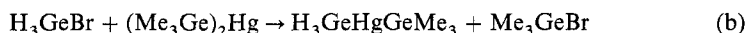
354      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.4. Ge—Group-IIB Bonds

**5.7.4.7. from Silyl- or Germylmercurials and Ge(IV) Halides.**

The only  $\text{GeCl}_4$  reaction under this heading is<sup>1</sup>:



Germyl bromide reacts with bis(trimethylgermyl)mercury to exchange either one or both  $\text{Me}_3\text{Ge}$  groups<sup>2</sup>:

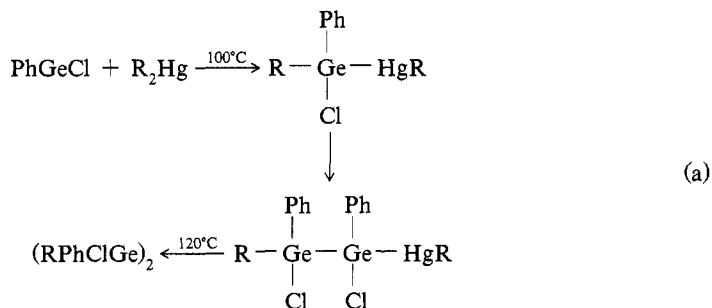


(F. GLOCKLING)

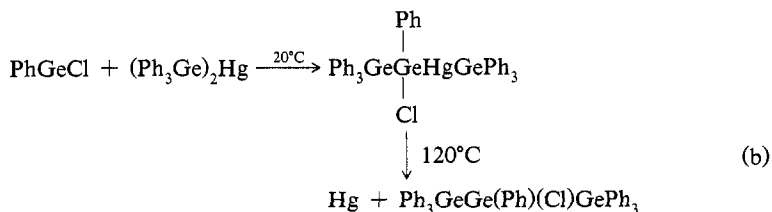
1. F. Glockling, J. J. Sweeney, *J. Chem. Res.*, (S), 35; (M) 615 (1977).
2. S. Cradock, E. A. V. Ebsworth, N. S. Hosmane, K. M. Mackay, *Angew. Chem., Int. Ed. Engl.*, 14, 167 (1975).

**5.7.4.8. by Insertion of Germylenes into Hg—C or Hg—Ge Bonds.**

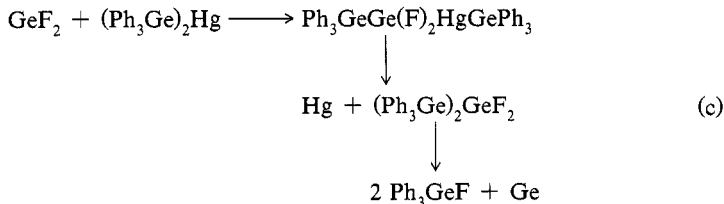
Germylenes (e.g.,  $\text{GeF}_2$ ,  $\text{PhGeCl}$ ,  $\text{R}_2\text{Ge}$ ) insert into both  $\text{Hg—C}$  and  $\text{Ge—Hg}$  bonds, the reactivity depending on the electrophilicity of the germylene ( $\text{GeX}_2 > \text{RGeX} > \text{R}_2\text{Ge}$ ), e.g.:



With bis(triphenylgermyl)mercury this reaction takes place at RT:







(F. GLOCKLING)

1. P. Rivière, A. Castel, J. Satgé, A. Cazes, private communication.
2. P. Rivière, A. Castel, J. Satgé, D. Guyot, *J. Organomet. Chem.*, 264, 193 (1984).

### 5.7.5. Tin–Group-IIB Bonds

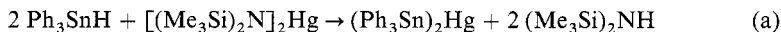
Most of these compounds are prepared by the hydride method, by hydrostannolysis of metal alkyls with organotin hydrides (see §5.7.5.2).

Another method proceeds directly from the elements. For Zn, intermediates containing Sn—Zn bonds form. Electrochemical syntheses produce  $\text{Ph}_3\text{SnMCl}$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) adducts. For reactions involving formation from the elements see §5.7.5.1.

Two other methods involve reacting organotin halides with germyl–Hg compounds (see §5.7.5.3) and organotin alkoxides with silyl–Hg compounds (see §5.7.5.4).

The reaction of  $\text{ZnCl}_2$  with  $\text{Ph}_3\text{SnK}$  in liq  $\text{NH}_3$ , followed by extraction with tetrahydrofuran (THF), yields<sup>1</sup> unsolvated  $(\text{Ph}_3\text{Sn})_2\text{Zn}$ .

The reaction of 2 : 1  $\text{Ph}_3\text{SnH}$  with  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Hg}$  at RT:

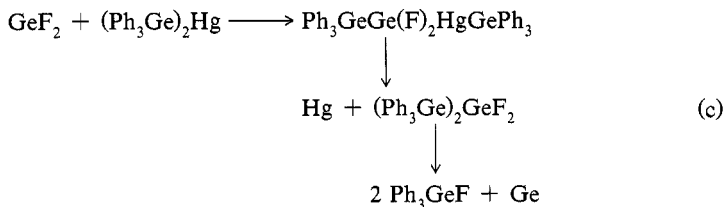


yields a bright-yellow, solid, stannyl–Hg product that is stable in the dark for months at RT but decomposes in daylight. It is less stable than the known organosilicon- or organogermanium–Hg analogues, and decomposes<sup>2</sup> in < 5 min in a sealed tube at 100°C.

Insertions yield a stable chain of four metal atoms<sup>3,4</sup>, Sn–Hg–Pt–Sn; e.g.,  $[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Hg}$  with  $\text{Pt}(\text{PPh}_3)_3$  in benzene under Ar gives  $(\text{C}_6\text{F}_5)_3\text{Sn—Hg—Pt}(\text{PPh}_3)_2\text{—Sn}(\text{C}_6\text{F}_5)_3 \cdot \text{C}_6\text{H}_6$ , greenish-yellow crystals that are stable in air and acids. This compound can be purified by chromatography on silica gel or by crystallization. It is soluble in benzene, THF or ethyl acetate, but solubility in hexane is low. The oligomeric chains resist heating in  $\text{CF}_3\text{COOH}$  for a short time. However, longer boiling in this acid (4 h) or UV irradiation in benzene (30 min) results in demercuration.

The product loses its benzene of crystallization on heating to 45–50°C under reduced pressure<sup>4</sup>.

The stannyl–Hg compounds,  $(\text{R}_3\text{Sn})_2\text{Hg}$ , have low thermal stability, but such R groups as t-Bu,  $\text{Me}_3\text{SiCH}_2$  and  $\text{PhMe}_2\text{CCH}_2$  stabilize the Sn—Hg bond. In the attempt to prepare  $(\text{C}_6\text{F}_5)_3\text{Sn—Hg—Sn}(\text{CH}_2\text{SiMe}_3)_3$ , which contains two such stabilizing groups in the same molecule, by the exchange on Hg metal of  $[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Hg}$  with



(F. GLOCKLING)

1. P. Rivière, A. Castel, J. Satgé, A. Cazes, private communication.
2. P. Rivière, A. Castel, J. Satgé, D. Guyot, *J. Organomet. Chem.*, **264**, 193 (1984).

### 5.7.5. Tin–Group-IIB Bonds

Most of these compounds are prepared by the hydride method, by hydrostannolysis of metal alkyls with organotin hydrides (see §5.7.5.2).

Another method proceeds directly from the elements. For Zn, intermediates containing Sn—Zn bonds form. Electrochemical syntheses produce  $\text{Ph}_3\text{SnMCl}$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) adducts. For reactions involving formation from the elements see §5.7.5.1.

Two other methods involve reacting organotin halides with germyl–Hg compounds (see §5.7.5.3) and organotin alkoxides with silyl–Hg compounds (see §5.7.5.4).

The reaction of  $\text{ZnCl}_2$  with  $\text{Ph}_3\text{SnK}$  in liq  $\text{NH}_3$ , followed by extraction with tetrahydrofuran (THF), yields<sup>1</sup> unsolvated  $(\text{Ph}_3\text{Sn})_2\text{Zn}$ .

The reaction of 2 : 1  $\text{Ph}_3\text{SnH}$  with  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Hg}$  at RT:



yields a bright-yellow, solid, stannyl–Hg product that is stable in the dark for months at RT but decomposes in daylight. It is less stable than the known organosilicon- or organogermanium–Hg analogues, and decomposes<sup>2</sup> in < 5 min in a sealed tube at 100°C.

Insertions yield a stable chain of four metal atoms<sup>3,4</sup>, Sn–Hg–Pt–Sn; e.g.,  $[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Hg}$  with  $\text{Pt}(\text{PPh}_3)_3$  in benzene under Ar gives  $(\text{C}_6\text{F}_5)_3\text{Sn—Hg—Pt}(\text{PPh}_3)_2\text{—Sn}(\text{C}_6\text{F}_5)_3 \cdot \text{C}_6\text{H}_6$ , greenish-yellow crystals that are stable in air and acids. This compound can be purified by chromatography on silica gel or by crystallization. It is soluble in benzene, THF or ethyl acetate, but solubility in hexane is low. The oligomeric chains resist heating in  $\text{CF}_3\text{COOH}$  for a short time. However, longer boiling in this acid (4 h) or UV irradiation in benzene (30 min) results in demercuration.

The product loses its benzene of crystallization on heating to 45–50°C under reduced pressure<sup>4</sup>.

The stannyl–Hg compounds,  $(\text{R}_3\text{Sn})_2\text{Hg}$ , have low thermal stability, but such R groups as t-Bu,  $\text{Me}_3\text{SiCH}_2$  and  $\text{PhMe}_2\text{CCH}_2$  stabilize the Sn—Hg bond. In the attempt to prepare  $(\text{C}_6\text{F}_5)_3\text{Sn—Hg—Sn}(\text{CH}_2\text{SiMe}_3)_3$ , which contains two such stabilizing groups in the same molecule, by the exchange on Hg metal of  $[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Hg}$  with

$[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Hg}$  in toluene in a 1 : 1 mole ratio at  $-20^\circ\text{C}$ , Hg (70 %) and the ditin,  $(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{CH}_2\text{SiMe}_3)_3$ , form instead in 65 % yield<sup>5</sup>.

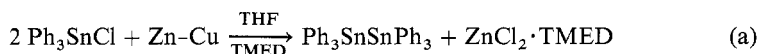
(A. K. SAWYER)

1. R. Egger, Ph.D. Thesis, Univ. München, 1961.
2. C. Eaborn, A. R. Thompson, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1051 (1968).
3. V. I. Sokolov, V. V. Bashilov, O. A. Reutov, M. N. Bochkarev, L. P. Maiorova, G. A. Razuvaev, *J. Organomet. Chem.*, 112, C47 (1976).
4. M. N. Bochkarev, G. A. Razuvaev, L. P. Maiorova, N. P. Makarenko, V. I. Sokolov, V. V. Bashilov, O. A. Reutov, *J. Organomet. Chem.*, 131, 399 (1977).
5. M. N. Bochkarev, N. S. Vyazankin, L. P. Maiorova, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, 48, 2454 (1978).

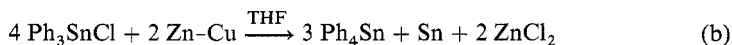
### 5.7.5.1. from the Elements

#### 5.7.5.1.1. with Zn.

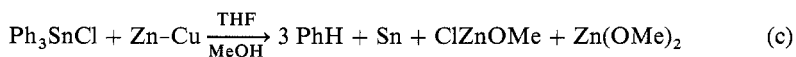
Although no alkyltin-zinc halide can be isolated, reactions of these halides with metallic Zn in the presence of organic bases gives products consistent with the formation of organotin-Zn halides as intermediates<sup>1</sup>. In the presence of the strongly chelating agents tetramethylethylenediamine (TMED) and bipy,  $\text{Ph}_3\text{SnCl}$  reacts with a Zn-Cu couple (prepared according to ref. 2) in refluxing tetrahydrofuran (THF) to form  $\text{Ph}_6\text{Sn}_2$  in 60–80 % yield<sup>3,4</sup>.



However, in the absence of TMED or bipy, the products of this reaction are  $\text{Ph}_4\text{Sn}$  (in 75–98 % yield) and metallic Sn:

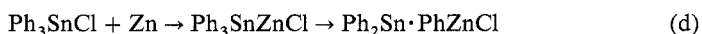


If reaction (b) is carried out in the presence of proton donors (e.g., MeOH,  $\text{H}_2\text{O}$ ), the products are benzene (in 90 % yield) and metallic Sn:

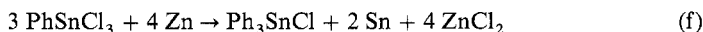
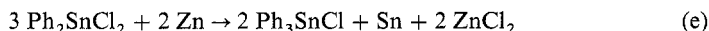


The primary intermediate is  $\text{Ph}_3\text{Sn-ZnCl}$  with the coordinating ligands influencing its reactivity.

The  $\text{Ph}_3\text{Sn-ZnCl}$  intermediate can be prepared separately, in both complexed and uncomplexed form, by the hydride method. In the absence of strongly coordinating ligands a 1,2-intermetallic shift occurs that, followed by other reactions, accounts for the observed products:



Reactions of  $\text{Me}_3\text{SnCl}$  and  $\text{Me}_2\text{PhSnCl}$  with Sn-Cu in THF under varying conditions are explained analogously. Unlike  $\text{Ph}_3\text{SnCl}$ , both  $\text{Ph}_2\text{SnCl}_2$  and  $\text{PhSnCl}_3$  react with unactivated Zn. In each case the product<sup>3</sup> is  $\text{Ph}_3\text{SnCl}$ :



356      5.7. Formation of Bonds between Elements of Groups IVB and IIB  
 5.7.5. Tin-Group-IIB Bonds

$[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Hg}$  in toluene in a 1 : 1 mole ratio at  $-20^\circ\text{C}$ , Hg (70%) and the ditin,  $(\text{C}_6\text{F}_5)_3\text{SnSn}(\text{CH}_2\text{SiMe}_3)_3$ , form instead in 65% yield<sup>5</sup>.

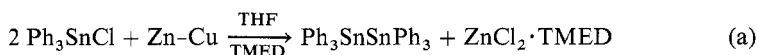
(A. K. SAWYER)

1. R. Egger, Ph.D. Thesis, Univ. München, 1961.
2. C. Eaborn, A. R. Thompson, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1051 (1968).
3. V. I. Sokolov, V. V. Bashilov, O. A. Reutov, M. N. Bochkarev, L. P. Maiorova, G. A. Razuvaev, *J. Organomet. Chem.*, 112, C47 (1976).
4. M. N. Bochkarev, G. A. Razuvaev, L. P. Maiorova, N. P. Makarenko, V. I. Sokolov, V. V. Bashilov, O. A. Reutov, *J. Organomet. Chem.*, 131, 399 (1977).
5. M. N. Bochkarev, N. S. Vyazankin, L. P. Maiorova, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, 48, 2454 (1978).

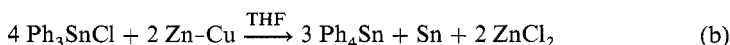
### 5.7.5.1. from the Elements

#### 5.7.5.1.1. with Zn.

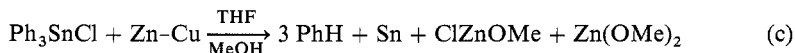
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However, in the absence of TMED or bipy, the products of this reaction are  $\text{Ph}_4\text{Sn}$  (in 75-98% yield) and metallic Sn:

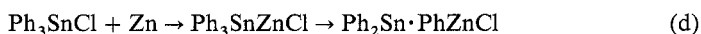


If reaction (b) is carried out in the presence of proton donors (e.g., MeOH,  $\text{H}_2\text{O}$ ), the products are benzene (in 90% yield) and metallic Sn:

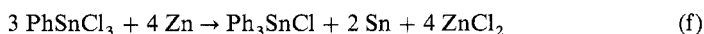
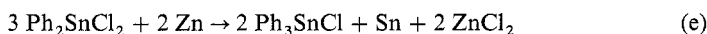


The primary intermediate is  $\text{Ph}_3\text{Sn-ZnCl}$  with the coordinating ligands influencing its reactivity.

The  $\text{Ph}_3\text{Sn-ZnCl}$  intermediate can be prepared separately, in both complexed and uncomplexed form, by the hydride method. In the absence of strongly coordinating ligands a 1,2-intermetallic shift occurs that, followed by other reactions, accounts for the observed products:



Reactions of  $\text{Me}_3\text{SnCl}$  and  $\text{Me}_2\text{PhSnCl}$  with Sn-Cu in THF under varying conditions are explained analogously. Unlike  $\text{Ph}_3\text{SnCl}$ , both  $\text{Ph}_2\text{SnCl}_2$  and  $\text{PhSnCl}_3$  react with unactivated Zn. In each case the product<sup>3</sup> is  $\text{Ph}_3\text{SnCl}$ :



When  $\text{Ph}_2\text{SnCl}_2$  or  $\text{PhSnCl}_3$  reacts with Zn-Cu,  $\text{Ph}_3\text{SnCl}$  is an intermediate, and organotin-Zn compounds form followed by 1,2- intermetallic shifts<sup>3-4</sup>.

However,  $\text{Ph}_3\text{SnZnCl}$  can be synthesized electrochemically and isolated as the TMED complex. Zinc is oxidized in non-aq  $\text{Ph}_3\text{SnCl}$  containing  $[\text{Et}_4\text{N}]\text{ClO}_4$  to give the  $\text{Ph}_3\text{SnZnCl}$  complex nearly quantitatively<sup>5</sup>.

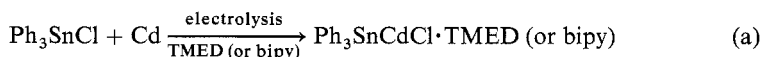
The scale can be increased. In a typical experiment the solid formed in the cell during electrolysis is collected and further quantities are obtained by adding petroleum ether dropwise to the filtrate<sup>6,7</sup>.

(A. K. SAWYER)

1. K. Sisido, S. Kozima, *J. Organomet. Chem.*, **11**, 503 (1968).
2. E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
3. F. J. A. des Tombe, G. J. M. van der Kerk, J. G. Noltes, *J. Organomet. Chem.*, **51**, 173 (1973).
4. F. J. A. des Tombe, G. J. M. van der Kerk, J. G. Noltes, *J. Organomet. Chem.*, **13**, P9 (1968).
5. J. J. Habeeb, A. Osman, D. G. Tuck, *Inorg. Chem. Acta*, **35**, 105 (1979).
6. J. J. Habeeb, A. Osman, D. G. Tuck, *J. Chem. Soc., Chem. Commun.*, 379 (1976).
7. J. J. Habeeb, D. G. Tuck, *J. Organomet. Chem.*, **146**, 213 (1978).

#### 5.7.5.1.2. with Cd.

The electrochemical oxidation of Cd in the presence of  $\text{Ph}_3\text{SnCl}$  in  $\text{CH}_3\text{CN}$ -benzene and in the presence of tetramethylethylenediamine (TMED) and bipy yields the corresponding adducts  $\text{Ph}_3\text{SnCdCl}\cdot\text{TMED}$  (in 30 % yield), and  $\text{Ph}_3\text{SnCdCl}\cdot\text{bipy}$  (in 43 % yield), respectively<sup>1</sup>:



This reaction is similar to that for Zn (see ref. 1, §5.7.5.1.1).

(A. K. SAWYER)

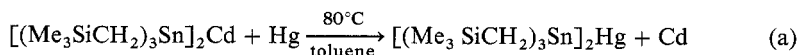
1. J. J. Habeeb, A. Osman, D. A. Tuck, *Inorg. Chem. Acta*, **35**, 105 (1979).

#### 5.7.5.1.3. with Hg.

Electrochemical oxidation of Hg in the presence of  $\text{Ph}_3\text{SnCl}$  in  $\text{CH}_3\text{CN}$ -benzene with bipy gives<sup>1</sup>  $\text{Ph}_3\text{SnHgCl}\cdot\text{bipy}$ , similarly to the Zn and Cd reactions (§5.7.5.1.1 and §5.7.5.1.2).

Attempts to make  $(\text{Ph}_3\text{Sn})_2\text{Hg}$  by the action of Na amalgam on  $\text{Ph}_3\text{SnBr}$  fail<sup>2</sup>.

One way of obtaining  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Hg}$  in high yield is from  $[(\text{Me}_3\text{SiCH}_2)_3]_2\text{Cd}$  in toluene by the action<sup>3</sup> of Hg metal:



(A. K. SAWYER)

1. J. J. Habeeb, A. Osman, D. A. Tuck, *Inorg. Chem. Acta.*, **35**, 105 (1979).
2. C. Eaborn, A. R. Thompson, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1051 (1968).
3. G. S. Kalinina, O. A. Kruglaya, B. I. Petrov, E. A. Shchupak, V. S. Vyazankin, *J. Gen. Chem. USSR, (Engl. Transl.)*, **43**, 2215 (1973).

5.7. Formation of Bonds between Elements of Groups IVB and IIB 357  
 5.7.5. Tin-Group-IIB Bonds  
 5.7.5.1. from the Elements

When  $\text{Ph}_2\text{SnCl}_2$  or  $\text{PhSnCl}_3$  reacts with Zn-Cu,  $\text{Ph}_3\text{SnCl}$  is an intermediate, and organotin-Zn compounds form followed by 1,2- intermetallic shifts<sup>3-4</sup>.

However,  $\text{Ph}_3\text{SnZnCl}$  can be synthesized electrochemically and isolated as the TMED complex. Zinc is oxidized in non-aq  $\text{Ph}_3\text{SnCl}$  containing  $[\text{Et}_4\text{N}]\text{ClO}_4$  to give the  $\text{Ph}_3\text{SnZnCl}$  complex nearly quantitatively<sup>5</sup>.

The scale can be increased. In a typical experiment the solid formed in the cell during electrolysis is collected and further quantities are obtained by adding petroleum ether dropwise to the filtrate<sup>6,7</sup>.

(A. K. SAWYER)

1. K. Sisido, S. Kozima, *J. Organomet. Chem.*, **11**, 503 (1968).
2. E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
3. F. J. A. des Tombe, G. J. M. van der Kerk, J. G. Noltes, *J. Organomet. Chem.*, **51**, 173 (1973).
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5. J. J. Habeeb, A. Osman, D. G. Tuck, *Inorg. Chem. Acta*, **35**, 105 (1979).
6. J. J. Habeeb, A. Osman, D. G. Tuck, *J. Chem. Soc., Chem. Commun.*, 379 (1976).
7. J. J. Habeeb, D. G. Tuck, *J. Organomet. Chem.*, **146**, 213 (1978).

**5.7.5.1.2. with Cd.**

The electrochemical oxidation of Cd in the presence of  $\text{Ph}_3\text{SnCl}$  in  $\text{CH}_3\text{CN}$ -benzene and in the presence of tetramethylethylenediamine (TMED) and bipy yields the corresponding adducts  $\text{Ph}_3\text{SnCdCl}\cdot\text{TMED}$  (in 30% yield), and  $\text{Ph}_3\text{SnCdCl}\cdot\text{bipy}$  (in 43% yield), respectively<sup>1</sup>:



This reaction is similar to that for Zn (see ref. 1, §5.7.5.1.1).

(A. K. SAWYER)

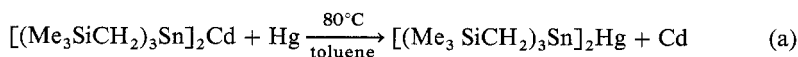
1. J. J. Habeeb, A. Osman, D. A. Tuck, *Inorg. Chem. Acta*, **35**, 105 (1979).

**5.7.5.1.3. with Hg.**

Electrochemical oxidation of Hg in the presence of  $\text{Ph}_3\text{SnCl}$  in  $\text{CH}_3\text{CN}$ -benzene with bipy gives<sup>1</sup>  $\text{Ph}_3\text{SnHgCl}\cdot\text{bipy}$ , similarly to the Zn and Cd reactions (§5.7.5.1.1 and §5.7.5.1.2).

Attempts to make  $(\text{Ph}_3\text{Sn})_2\text{Hg}$  by the action of Na amalgam on  $\text{Ph}_3\text{SnBr}$  fail<sup>2</sup>.

One way of obtaining  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Hg}$  in high yield is from  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Cd}$  in toluene by the action<sup>3</sup> of Hg metal:



(A. K. SAWYER)

1. J. J. Habeeb, A. Osman, D. A. Tuck, *Inorg. Chem. Acta*, **35**, 105 (1979).
2. C. Eaborn, A. R. Thompson, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1051 (1968).
3. G. S. Kalinina, O. A. Kruglaya, B. I. Petrov, E. A. Shchupak, V. S. Vyazankin, *J. Gen. Chem. USSR, (Engl. Transl.)*, **43**, 2215 (1973).

5.7. Formation of Bonds between Elements of Groups IVB and IIB 357  
 5.7.5. Tin–Group-IIB Bonds  
 5.7.5.1. from the Elements

When  $\text{Ph}_2\text{SnCl}_2$  or  $\text{PhSnCl}_3$  reacts with  $\text{Zn–Cu}$ ,  $\text{Ph}_3\text{SnCl}$  is an intermediate, and organotin–Zn compounds form followed by 1,2- intermetallic shifts<sup>3–4</sup>.

However,  $\text{Ph}_3\text{SnZnCl}$  can be synthesized electrochemically and isolated as the TMED complex. Zinc is oxidized in non-aq  $\text{Ph}_3\text{SnCl}$  containing  $[\text{Et}_4\text{N}]\text{ClO}_4$  to give the  $\text{Ph}_3\text{SnZnCl}$  complex nearly quantitatively<sup>5</sup>.

The scale can be increased. In a typical experiment the solid formed in the cell during electrolysis is collected and further quantities are obtained by adding petroleum ether dropwise to the filtrate<sup>6,7</sup>.

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7. J. J. Habeeb, D. G. Tuck, *J. Organomet. Chem.*, **146**, 213 (1978).

**5.7.5.1.2. with Cd.**

The electrochemical oxidation of Cd in the presence of  $\text{Ph}_3\text{SnCl}$  in  $\text{CH}_3\text{CN}$ –benzene and in the presence of tetramethylethylenediamine (TMED) and bipy yields the corresponding adducts  $\text{Ph}_3\text{SnCdCl}\cdot\text{TMED}$  (in 30 % yield), and  $\text{Ph}_3\text{SnCdCl}\cdot\text{bipy}$  (in 43 % yield), respectively<sup>1</sup>:



This reaction is similar to that for Zn (see ref. 1, §5.7.5.1.1).

(A. K. SAWYER)

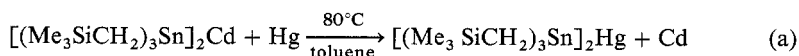
1. J. J. Habeeb, A. Osman, D. A. Tuck, *Inorg. Chem. Acta*, **35**, 105 (1979).

**5.7.5.1.3. with Hg.**

Electrochemical oxidation of Hg in the presence of  $\text{Ph}_3\text{SnCl}$  in  $\text{CH}_3\text{CN}$ –benzene with bipy gives<sup>1</sup>  $\text{Ph}_3\text{SnHgCl}\cdot\text{bipy}$ , similarly to the Zn and Cd reactions (§5.7.5.1.1 and §5.7.5.1.2).

Attempts to make  $(\text{Ph}_3\text{Sn})_2\text{Hg}$  by the action of Na amalgam on  $\text{Ph}_3\text{SnBr}$  fail<sup>2</sup>.

One way of obtaining  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Hg}$  in high yield is from  $[(\text{Me}_3\text{SiCH}_2)_3]_2\text{Cd}$  in toluene by the action<sup>3</sup> of Hg metal:



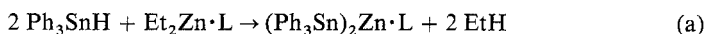
(A. K. SAWYER)

1. J. J. Habeeb, A. Osman, D. A. Tuck, *Inorg. Chem. Acta.*, **35**, 105 (1979).
2. C. Eaborn, A. R. Thompson, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1051 (1968).
3. G. S. Kalinina, O. A. Kruglaya, B. I. Petrov, E. A. Shchupak, V. S. Vyazankin, *J. Gen. Chem. USSR, (Engl. Transl.)*, **43**, 2215 (1973).

**5.7.5.2. from Organotin Hydrides with Zn, Cd and Hg Dialkyls****5.7.5.2.1. with Zn Alkyls.**

Most Sn—Zn bonds are prepared by the hydride method, i.e., hydrostannolysis using an organotin hydride and a dialkylzinc or alkylzinc halide, either complexed or uncomplexed.

The reaction of  $\text{Et}_3\text{SnH}$  with  $\text{Et}_2\text{Zn}$  results in decomposition with the formation of Zn metal, ethane, tetraethyltin, hexaethylditin and a polymer<sup>1</sup>. The reaction of  $\text{Ph}_3\text{SnH}$  with  $\text{Et}_2\text{Zn}$  in pentane or benzene forms<sup>2</sup> metallic Zn. However, when hydrostannolysis is carried out with preformed complexes of  $\text{Et}_2\text{Zn}$  or with a complexing solvent, such as 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF), or by using a preformed coordination complex of  $\text{Et}_2\text{Zn}$  with tetramethylethylenediamine (TMED) or bipy, the bis(triphenyltin)zinc complexes are obtained in high yields under mild conditions ( $-20^\circ$  to  $0^\circ\text{C}$ )<sup>2,3</sup>:



where L = THF, DME, TMED or bipy. Coordination saturation not only promotes reaction because of the enhanced nucleophilicity of the R group but also contributes to the stability of the products. Attempts to remove THF from the bis(triphenyltin)-zinc·THF complex at  $50^\circ\text{C}$  and  $10^{-3}$  torr ( $10^{-1}$  Pa) result in gradual decomposition with metal deposition, whereas the TMED complex melts at  $173^\circ\text{C}$  without deposition of metal.

These complexes are prepared as crystals that slowly decompose on exposure to air (see Table 1).

When  $\text{EtZnCl}$  is used instead of  $\text{Et}_2\text{Zn}$  in these hydrostannolyses with  $\text{Ph}_3\text{SnH}$ , and under the same conditions, selective hydrostannolysis of the Zn—C bond occurs to form (triphenyltin)zinc chloride complexes (see Table 1)<sup>4</sup>:



where L =  $\text{Et}_2\text{O}$ , DME or TMED.

Uncomplexed (triphenyltin)zinc chloride is obtained from the  $\text{Et}_2\text{O}$  complex when the latter is heated for 6 h at  $70^\circ\text{C}$  in vacuo ( $10^{-3}$  torr,  $10^{-1}$  Pa) to constant weight. It is a dimer,  $(\text{Ph}_3\text{SnZnCl})_2$ , in boiling benzene<sup>4,5</sup>.

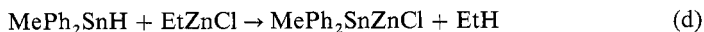
TABLE 1. COMPOUNDS CONTAINING Sn—Zn BONDS PREPARED BY THE HYDRIDE METHOD

Compound	Yield (%)	mp ( $^\circ\text{C}$ )	Color	Refs.
$(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{TMED}$	84	172.5–174	White	2,3
$(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{bipy}$	85	141.5–144	Red	2,3
$(\text{Ph}_3\text{Sn})_2\text{Zn} \cdot \text{DME}$	48	103.5–104	White	2,3
$(\text{MePh}_2\text{Sn})_2\text{Zn} \cdot \text{TMED}$	62	121–123	a	4
$(\text{Ph}_3\text{SnZnCl})_2$	60	102–105 (decomp without melting)	Yellow	4,5
$\text{Ph}_3\text{SnZnCl} \cdot \text{TMED}$	87.5	164–165	White	2,4
$\text{Ph}_3\text{SnZnCl} \cdot \text{DME}$	61.0	73–76	a	2,4

a Not indicated.



Whereas attempts to prepare (trialkyltin)zincs by hydrostannolysis of ethylzincs by trialkyltin hydrides fail,  $\text{MePh}_2\text{SnH}$  yields such compounds from  $\text{Et}_2\text{Zn} \cdot \text{TMED}$  and  $\text{EtZnCl}^4$ :



Although the  $(\text{MePh}_2\text{Sn})_2\text{Zn} \cdot \text{TMED}$  complex has been isolated and characterized,  $\text{MePh}_2\text{SnZnCl}$  is prepared in situ in THF and used without isolation.

(A. K. SAWYER)

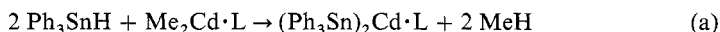
1. N. S. Vyazankin, G. A. Razuvaev, S. P. Korneva, O. A. Kruglaya, R. F. Guliulina, *Dokl. Chem. (Engl. Transl.)* 158, 884 (1964).
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4. F. J. A. des Tombe, G. J. M. van der Kerk, J. G. Noltes, *J. Organomet. Chem.*, 43, 323 (1972).
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#### 5.7.5.2.2. with Cd Alkyls.

Most Sn—Cd bond-containing compounds capable of isolation are prepared by the hydride method, i.e., hydrostannolysis using an organotin hydride with the appropriate  $\text{R}_2\text{Cd}$  or alkylcadmium halide, either complexed or uncomplexed.

The reaction of  $\text{Ph}_3\text{SnH}$  with  $\text{Me}_2\text{Cd}$  forms<sup>1</sup> metallic Cd.

However, at  $-40^\circ\text{C}$ , and with 1 mM concentrations of Cd, excellent yields are obtained by carrying out the hydrostannolysis in  $\text{Et}_2\text{O}$ , tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) or by using a preformed coordination complex of  $\text{Me}_2\text{Cd}$  [e.g., with tetramethylethylenediamine (TMED), or bipy] (see Table 1)<sup>1,2</sup>:



where L = TMED or bipy. As with Zn, coordination saturation of Cd not only promotes reaction but also contributes to the stability of the products.

Similarly  $\text{MeCdCl}$ , obtained from equimolar  $\text{Me}_2\text{Cd}$  and  $\text{CdCl}_2$  in dimethylsulfoxide (DMSO) and not isolated either in the solvated form or as a preformed complex<sup>1,3</sup>,

TABLE 1. COMPOUNDS CONTAINING Sn—Cd BONDS PREPARED BY THE HYDRIDE METHOD

Compound	Yield (%)	mp ( $^\circ\text{C}$ )	Color	Refs.
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{TMED}$	85	175 (decomp)	White	1-3
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{bipy}$	87	154 (decomp)	Orange	1-3
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{DME}$	30	110 (decomp)	White	1-3
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot 1,10\text{-phen}$	86	190 (decomp)	Orange	3
$\text{Ph}_3\text{SnCdCl} \cdot \text{TMED}$	82	175 (decomp)	a	1,3
$[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Cd}$	a	120-125 (decomp)	White	5
$[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Cd}$	83	96-99	Green-yellow	4
$[(\text{Me}_3\text{CCH}_2)_3\text{Sn}]_2\text{Cd}$	a	a	a	6

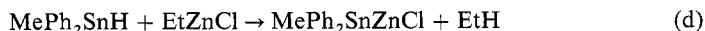
<sup>a</sup> Not indicated.

## 5.7. Formation of Bonds between Elements of Groups IVB and IIB 359

## 5.7.5. Tin—Group-IIB Bonds

## 5.7.5.2. from Organotin Hydrides with Zn, Cd and Hg Dialkyls

Whereas attempts to prepare (trialkyltin)zincs by hydrostannolysis of ethylzincs by trialkyltin hydrides fail,  $\text{MePh}_2\text{SnH}$  yields such compounds from  $\text{Et}_2\text{Zn} \cdot \text{TMED}$  and  $\text{EtZnCl}^4$ :



Although the  $(\text{MePh}_2\text{Sn})_2\text{Zn} \cdot \text{TMED}$  complex has been isolated and characterized,  $\text{MePh}_2\text{SnZnCl}$  is prepared in situ in THF and used without isolation.

(A. K. SAWYER)

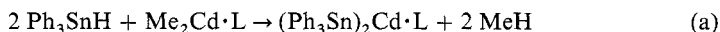
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## 5.7.5.2.2. with Cd Alkyls.

Most Sn—Cd bond-containing compounds capable of isolation are prepared by the hydride method, i.e., hydrostannolysis using an organotin hydride with the appropriate  $\text{R}_2\text{Cd}$  or alkylcadmium halide, either complexed or uncomplexed.

The reaction of  $\text{Ph}_3\text{SnH}$  with  $\text{Me}_2\text{Cd}$  forms<sup>1</sup> metallic Cd.

However, at  $-40^\circ\text{C}$ , and with 1 mM concentrations of Cd, excellent yields are obtained by carrying out the hydrostannolysis in  $\text{Et}_2\text{O}$ , tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) or by using a preformed coordination complex of  $\text{Me}_2\text{Cd}$  [e.g., with tetramethylethylenediamine (TMED), or bipy] (see Table 1)<sup>1,2</sup>:



where L = TMED or bipy. As with Zn, coordination saturation of Cd not only promotes reaction but also contributes to the stability of the products.

Similarly  $\text{MeCdCl}$ , obtained from equimolar  $\text{Me}_2\text{Cd}$  and  $\text{CdCl}_2$  in dimethylsulfoxide (DMSO) and not isolated either in the solvated form or as a preformed complex<sup>1,3</sup>,

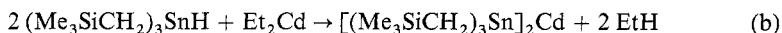
TABLE 1. COMPOUNDS CONTAINING Sn—Cd BONDS PREPARED BY THE HYDRIDE METHOD

Compound	Yield (%)	mp ( $^\circ\text{C}$ )	Color	Refs.
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{TMED}$	85	175 (decomp)	White	1–3
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{bipy}$	87	154 (decomp)	Orange	1–3
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot \text{DME}$	30	110 (decomp)	White	1–3
$(\text{Ph}_3\text{Sn})_2\text{Cd} \cdot 1,10\text{-phen}$	86	190 (decomp)	Orange	3
$\text{Ph}_3\text{SnCdCl} \cdot \text{TMED}$	82	175 (decomp)	a	1,3
$[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Cd}$	a	120–125 (decomp)	White	5
$[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Cd}$	83	96–99	Green-yellow	4
$[(\text{Me}_3\text{CCH}_2)_3\text{Sn}]_2\text{Cd}$	a	a	a	6

<sup>a</sup> Not indicated.

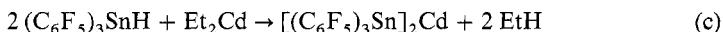
undergoes selective hydrostannolysis of the Cd—C bond, yielding the corresponding triphenyltin cadmium chloride complex (see Table 1).

The  $\text{Me}_3\text{SiCH}_2$  group enhances the stability of compounds with Sn—Cd bonds; e.g., although  $(\text{Ph}_3\text{Sn})_2\text{Cd}$  is unstable except when complexed,  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Cd}$  is stable uncomplexed. It is formed by the hydride reaction<sup>4</sup>:



After 2 h at RT ethane is obtained in quantitative yield, and the greenish-yellow product is decanted from traces of Cd and crystallized in 83 % yield.

Likewise, colorless  $[(\text{C}_6\text{F}_5)_3]_2\text{Cd}$  can be prepared<sup>5</sup> by the hydride method from  $(\text{C}_6\text{F}_5)_3\text{SnH}$  and  $\text{Et}_2\text{Cd}$ :



In hexane at 20°C over 30 min, ethane is formed in 90 % yield. When heated rapidly the distannylcadmium melts with decomposition at 122–125°C. Its decomposition with the liberation of Cd goes on even at RT, and attempts to isolate it pure fail.

A thermally stable neopentylstannylcadmium is obtained<sup>6</sup> by hydrostannolysis of  $\text{Et}_2\text{Cd}$  with the corresponding organotin hydride at 20°C for 2 h:



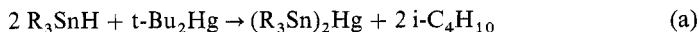
(A. K. SAWYER)

1. F. J. A. des Tombe, G. J. M. van der Kerk, H. M. J. C. Creemers, J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 914 (1966).
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### 5.7.5.2.3. with Hg Alkyls.

Reaction of  $\text{Et}_3\text{SnH}$  with  $(\text{PhCH}_2)_2\text{Hg}$  at 100°C fails to give compounds containing Sn—Hg bonds. Instead, Hg, ethane and  $\text{Et}_3\text{SnSnEt}_3$  are obtained<sup>1</sup>.

When  $t\text{-Bu}_2\text{Hg}$  reacts with trialkyltin hydrides at 30°C hydrostannolysis occurs<sup>2,3</sup> yielding the corresponding  $(\text{R}_3\text{Sn})_2\text{Hg}$ :



where R = Me, Et, n-Pr, t-Bu or Ph. The  $(\text{R}_3\text{Sn})_2\text{Hg}$  oxidizes in air and decompose at  $-10^\circ\text{C}$  into distannanes and Hg. The compound  $(\text{Ph}_3\text{Sn})_2\text{Hg}$  prepared by Eq. (a) is more stable thermally, decomposing at 20°C, but crystalline  $(t\text{-Bu}_3\text{Sn})_2\text{Hg}$  melts<sup>3</sup> at 196°C (see Table 1). When  $\text{Et}_2\text{Hg}$  is used instead of  $t\text{-Bu}_2\text{Hg}$  as in Eq. (a), only decomposition occurs<sup>2</sup>.

It is not necessary to isolate the  $(\text{R}_3\text{Sn})_2\text{Hg}$ . It is preferable to mix the reactant with  $t\text{-Bu}_2\text{Hg}$  (or  $\text{R}_3\text{SnH}$ ) and then slowly to add  $\text{R}_3\text{SnH}$  (or  $t\text{-Bu}_2\text{Hg}$ , respectively) at  $-20^\circ\text{C}$ . When  $t\text{-Bu}_2\text{Hg}$  reacts with  $\text{R}_2\text{SnH}_2$  (R = Et, n-Bu, i-Bu, t-Bu, cyclohexyl or Ph)

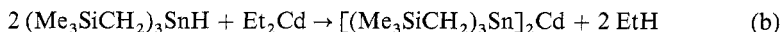
## 5.7. Formation of Bonds between Elements of Groups IVB and IIB

## 5.7.5. Tin-Group-IIB Bonds

## 5.7.5.2 from Organotin Hydrides with Zn, Cd and Hg Dialkyls

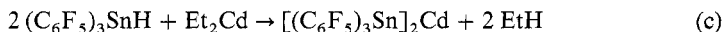
undergoes selective hydrostannolysis of the Cd—C bond, yielding the corresponding triphenyltin cadmium chloride complex (see Table 1).

The  $\text{Me}_3\text{SiCH}_2$  group enhances the stability of compounds with Sn—Cd bonds; e.g., although  $(\text{Ph}_3\text{Sn})_2\text{Cd}$  is unstable except when complexed,  $[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Cd}$  is stable uncomplexed. It is formed by the hydride reaction<sup>4</sup>:



After 2 h at RT ethane is obtained in quantitative yield, and the greenish-yellow product is decanted from traces of Cd and crystallized in 83 % yield.

Likewise, colorless  $[(\text{C}_6\text{F}_5)_3\text{Sn}]_2\text{Cd}$  can be prepared<sup>5</sup> by the hydride method from  $(\text{C}_6\text{F}_5)_3\text{SnH}$  and  $\text{Et}_2\text{Cd}$ :



In hexane at 20°C over 30 min, ethane is formed in 90 % yield. When heated rapidly the distannylcadmium melts with decomposition at 122–125°C. Its decomposition with the liberation of Cd goes on even at RT, and attempts to isolate it pure fail.

A thermally stable neopentylstannylcadmium is obtained<sup>6</sup> by hydrostannolysis of  $\text{Et}_2\text{Cd}$  with the corresponding organotin hydride at 20°C for 2 h:



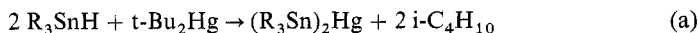
(A. K. SAWYER)

1. F. J. A. des Tombe, G. J. M. van der Kerk, H. M. J. C. Creemers, J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 914 (1966).
2. F. J. A. des Tombe, G. J. M. van der Kerk, H. M. J. D. Creemers, N. A. D. Carey, J. G. Noltes, *J. Organomet. Chem.*, **44**, 247 (1972).
3. H. M. J. C. Creemers, Ph.D. Thesis, State University of Utrecht, 1967.
4. G. S. Kalinina, O. A. Kruglaya, B. I. Petrov, E. A. Shchupak, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **43**, 2215 (1973).
5. M. N. Bochkarev, N. S. Vyazankin, L. P. Maiorova, G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, **48**, 2454 (1978).
6. B. V. Fedot'ev, O. A. Kruglaya, N. S. Vyazankin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 713 (1974).

## 5.7.5.2.3. with Hg Alkyls.

Reaction of  $\text{Et}_3\text{SnH}$  with  $(\text{PhCH}_2)_2\text{Hg}$  at 100°C fails to give compounds containing Sn—Hg bonds. Instead, Hg, ethane and  $\text{Et}_3\text{SnSnEt}_3$  are obtained<sup>1</sup>.

When  $t\text{-Bu}_2\text{Hg}$  reacts with trialkyltin hydrides at 30°C hydrostannolysis occurs<sup>2,3</sup> yielding the corresponding  $(\text{R}_3\text{Sn})_2\text{Hg}$ :



where R = Me, Et, n-Pr, t-Bu or Ph. The  $(\text{R}_3\text{Sn})_2\text{Hg}$  oxidizes in air and decompose at –10°C into distannanes and Hg. The compound  $(\text{Ph}_3\text{Sn})_2\text{Hg}$  prepared by Eq. (a) is more stable thermally, decomposing at 20°C, but crystalline  $(t\text{-Bu}_3\text{Sn})_2\text{Hg}$  melts<sup>3</sup> at 196°C (see Table 1). When  $\text{Et}_2\text{Hg}$  is used instead of  $t\text{-Bu}_2\text{Hg}$  as in Eq. (a), only decomposition occurs<sup>2</sup>.

It is not necessary to isolate the  $(\text{R}_3\text{Sn})_2\text{Hg}$ . It is preferable to mix the reactant with  $t\text{-Bu}_2\text{Hg}$  (or  $\text{R}_3\text{SnH}$ ) and then slowly to add  $\text{R}_3\text{SnH}$  (or  $t\text{-Bu}_2\text{Hg}$ , respectively) at –20°C. When  $t\text{-Bu}_2\text{Hg}$  reacts with  $\text{R}_2\text{SnH}_2$  (R = Et, n-Bu, i-Bu, t-Bu, cyclohexyl or Ph)

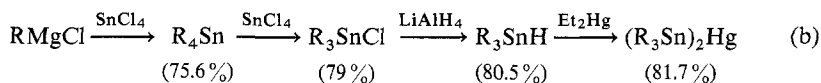
TABLE 1. COMPOUNDS CONTAINING Sn—Hg BONDS PREPARED BY THE HYDRIDE METHOD

Compound	Yield (%)	mp (°C)	Color	Ref.
		(or decomp pt)		
(Me <sub>3</sub> Sn) <sub>2</sub> Hg	75	— 10 (decomp)	Deep red needles	2,3
(Et <sub>3</sub> Sn) <sub>2</sub> Hg	70–75	— 10 (decomp)	Yellow liquid	2,3
(iPr <sub>3</sub> Sn) <sub>2</sub> Hg	70	— 10 (decomp)	Yellow liquid	3
(n-Bu <sub>3</sub> Sn) <sub>2</sub> Hg	50–70	— 10 (decomp)	Yellow liquid	2
(t-Bu <sub>3</sub> Sn) <sub>2</sub> Hg	90–95	196	Deep yellow crystals	3
(Ph <sub>3</sub> Sn) <sub>2</sub> Hg	50–80	20 (decomp)	Yellow solid	3
[(Me <sub>3</sub> SiCH <sub>2</sub> ) <sub>3</sub> Sn] <sub>2</sub> Hg	81	101–103	Pale yellow crystals	4
[(Me <sub>3</sub> CCH <sub>2</sub> ) <sub>3</sub> Sn] <sub>2</sub> Hg	71	a	Yellow	7
[(PhMe <sub>2</sub> CCH <sub>2</sub> ) <sub>3</sub> Sn] <sub>2</sub> Hg	a	114	Yellow crystals	5
[(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> Sn] <sub>2</sub> Hg	48	169–170	Colorless crystals	6
(t-Bu <sub>2</sub> Sn—Hg) <sub>n</sub>	100	a	Deep red solid	3

<sup>a</sup> Not indicated

a (R<sub>2</sub>Sn—Hg)<sub>n</sub> intermediate is formed that is stable only with R = t-Bu. In other cases decomposition occurs to form Hg and a mixture of cyclostannanes<sup>3</sup>.

The presence of the Me<sub>3</sub>SiCH<sub>2</sub> group as a substituent stabilizes (R<sub>3</sub>Sn)<sub>2</sub>Hg compounds. The compound [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg is prepared by<sup>4</sup>:

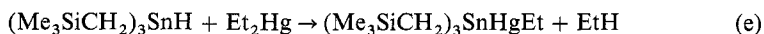


where R = Me<sub>3</sub>SiCH<sub>2</sub>. The stannylmercurial is stable both as the solid (mp 101°C) and in tetrahydrofuran (THF) or n-hexane. Heating at ca. 150°C for 10 h gives Hg metal almost quantitatively along with metallic Sn (76.2%) and (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>4</sub>Sn (in 65.0% yield). The decomposition proceeds by formation of the ditin followed by disproportionation:



Exposure of the stannylmercurial in THF to air for 1 h results in oxidation to the corresponding stannoxane, [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>O (73.6%) and Hg metal (in 97.3% yield).

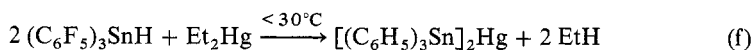
Despite a 2 : 1 (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>SnH : Et<sub>2</sub>Hg ratio, the replacement of ethyl groups in Et<sub>2</sub>Hg occurs stepwise to give an intermediate compound containing an Sn—Hg bond:



Such reactions are known in organosilicon and organogermanium chemistry. However, when the reaction is carried out in a 1 : 1 ratio, only the symmetrical mercurial, [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg, is isolated.

For studies on organotin-centered radicals, [(PhMe<sub>2</sub>CCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg is prepared from (PhMe<sub>2</sub>CCH<sub>2</sub>)<sub>3</sub>SnH and t-Bu<sub>2</sub>Hg in a 2 : 1 hydride : alkylmercury ratio. The yellow, crystalline product, mp 114°C, is a source of the [(PhMe<sub>2</sub>CCH<sub>2</sub>)<sub>3</sub>Sn] radical<sup>5</sup>.

The hydride method is used to prepare  $[(C_6F_5)_3Sn]_2Hg$  as shown. When the reagents are mixed at RT a vigorous exothermic reaction liberates ethane and precipitates crystals in 48 % yield (mp, 169°C)<sup>6</sup>:



A thermally stable neopentylstannylmercurial is obtained by hydrostannolysis of  $Et_2Hg$  with the corresponding organotin hydride:



The reaction is carried out for 2 h at 20°C to give the stannylmercurial in 71 % yield<sup>7</sup>.

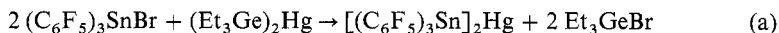
(A. K. SAWYER)

1. N. S. Vyazankin, G. A. Razuveav, S. P. Korneva, *J. Gen. Chem. USSR (Engl. Transl.)*, **34**, 2787 (1964).
2. W. P. Neumann, U. Blaukat, *Angew. Chem., Int. Ed. Engl.*, **8**, 611 (1969).
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4. O. A. Kruglaya, G. S. Kalinina, B. I. Petrov, N. S. Vyazankin, *J. Organomet. Chem.*, **46**, 51 (1972).
5. H. U. Bushlaus, M. Heknig, W. P. Neumann, *J. Chem. Soc., Chem. Commun.*, 129, (1977).
6. M. N. Bochkarev, N. S. Vyazankin, L. P. Maiorova, G. A. Razuveav, *J. Gen. Chem. USSR (Engl. Transl.)*, **48**, 2454 (1978).
7. B. V. Fedot'ev, O. A. Kruglaya, N. S. Vyazankin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 713 (1974).

### 5.7.5.3. from Organotin Halides with Germylmercurials.

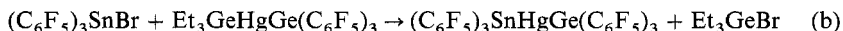
The reaction of 2 : 1  $(C_6F_5)_3SnBr$  (I) and  $(Et_3Ge)_2Hg$  (II) in toluene at 20°C for 3 h forms<sup>1</sup>  $Et_3GeBr$  (90 %), Hg metal (73 %) and  $(C_6F_5)_3SnSn(C_6F_5)_3$  (in 80 % yield) instead of the expected  $[(C_6F_5)_3Sn]_2Hg$ .

However, when 2 : 1 (I) and (II) in toluene is exposed to 365-nm radiation for 1 h at 20°C,  $[(C_6F_5)_3Sn]_2Hg$  results<sup>2,3</sup> in 58 % yield:



The colorless, crystalline stannylmercurial, mp 171°C, is slowly demercurated at > 80°-90°C.

Similarly, when 365-nm radiation is used after 30 min at 20°C, an Sn-Hg-Ge grouping is obtained by exchange, e.g.



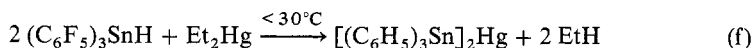
These colorless crystals, mp 205°C, have high thermal stability<sup>2,3</sup>.

(A. K. SAWYER)

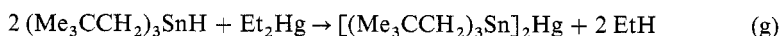
1. M. N. Bochkarev, N. S. Vyazankin, L. P. Maiorova, *Dokl. Chem. (Engl. Transl.)*, **200**, 1102 (1971).
2. M. N. Bochkarev, L. P. Maiorova, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **42**, 2344 (1972).
3. M. N. Bochkarev, S. P. Korneva, L. P. Maiorova, V. A. Kuznetsov, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **44**, 293 (1974).

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 5.7.5. Tin–Group-IIB Bonds

The hydride method is used to prepare  $[(C_6F_5)_3Sn]_2Hg$  as shown. When the reagents are mixed at RT a vigorous exothermic reaction liberates ethane and precipitates crystals in 48 % yield (mp, 169°C)<sup>6</sup>:



A thermally stable neopentylstannylmercurial is obtained by hydrostannolysis of  $Et_2Hg$  with the corresponding organotin hydride:



The reaction is carried out for 2 h at 20°C to give the stannylmercurial in 71 % yield<sup>7</sup>.

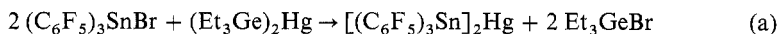
(A. K. SAWYER)

1. N. S. Vyazankin, G. A. Razuveav, S. P. Korneva, *J. Gen. Chem. USSR (Engl. Transl.)*, **34**, 2787 (1964).
2. W. P. Neumann, U. Blaukat, *Angew. Chem., Int. Ed. Engl.*, **8**, 611 (1969).
3. U. Blaukat, W. P. Neumann, *J. Organomet. Chem.*, **63**, 27 (1973).
4. O. A. Kruglaya, G. S. Kalinina, B. I. Petrov, N. S. Vyazankin, *J. Organomet. Chem.*, **46**, 51 (1972).
5. H. U. Bushlaus, M. Heknig, W. P. Neumann, *J. Chem. Soc., Chem. Commun.*, 129, (1977).
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7. B. V. Fedot'ev, O. A. Kruglaya, N. S. Vyazankin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 713 (1974).

### 5.7.5.3. from Organotin Halides with Germylmercurials.

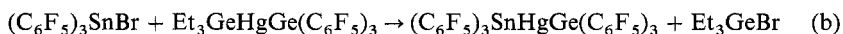
The reaction of 2 : 1  $(C_6F_5)_3SnBr$  (I) and  $(Et_3Ge)_2Hg$  (II) in toluene at 20°C for 3 h forms<sup>1</sup>  $Et_3GeBr$  (90 %), Hg metal (73 %) and  $(C_6F_5)_3SnSn(C_6F_5)_3$  (in 80 % yield) instead of the expected  $[(C_6F_5)_3Sn]_2Hg$ .

However, when 2 : 1 (I) and (II) in toluene is exposed to 365-nm radiation for 1 h at 20°C,  $[(C_6F_5)_3Sn]_2Hg$  results<sup>2,3</sup> in 58 % yield:



The colorless, crystalline stannylmercurial, mp 171°C, is slowly demercurated at > 80°–90°C.

Similarly, when 365-nm radiation is used after 30 min at 20°C, an Sn–Hg–Ge grouping is obtained by exchange, e.g.



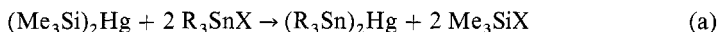
These colorless crystals, mp 205°C, have high thermal stability<sup>2,3</sup>.

(A. K. SAWYER)

1. M. N. Bochkarev, N. S. Vyazankin, L. P. Maiorova, *Dokl. Chem. (Engl. Transl.)*, **200**, 1102 (1971).
2. M. N. Bochkarev, L. P. Maiorova, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **42**, 2344 (1972).
3. M. N. Bochkarev, S. P. Korneva, L. P. Maiorova, V. A. Kuznetsov, N. S. Vyazankin, *J. Gen. Chem. USSR (Engl. Transl.)*, **44**, 293 (1974).

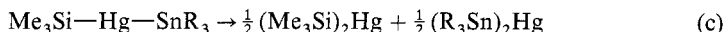
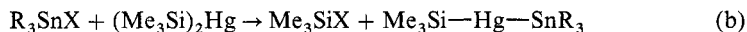
#### 5.7.5.4. from Organotin Alkoxides with Silylmercurials.

At  $-30^{\circ}\text{C}$  and at 0.1 torr (10 Pa)  $(\text{Me}_3\text{Si})_2\text{Hg}$  undergoes redistribution with trialkyltin alkoxides to form  $(\text{R}_3\text{Sn})_2\text{Hg}$  in high yield<sup>1</sup>:

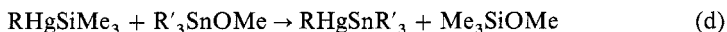


where R = Me, Et or Bu (unspecified isomer) and X = OR, OSiR<sub>3</sub>, OSnR<sub>3</sub> or NR<sub>2</sub>. At  $> 5^{\circ}\text{C}$  decomposition occurs, giving Hg and the corresponding ditin quantitatively.

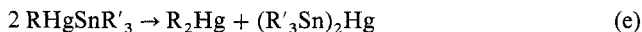
The reaction takes place stepwise, involving the formation of an unsymmetrical mercurial that undergoes symmetrization, e.g.<sup>2,3</sup>:



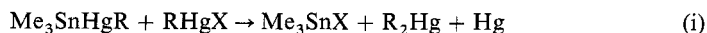
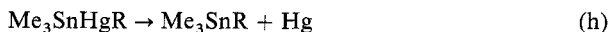
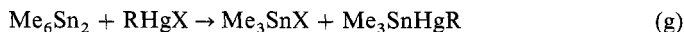
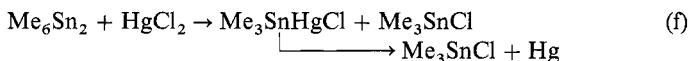
Redistribution yields trialkyltinalkylmercurials,  $\text{RHgSnR}'_3$ , e.g.:



The driving force of the reaction is the stability of the Si—O bond compared to the Sn—O bond in the alkoxide. The organostannylalkylmercury products are yellow to orange viscous liquids<sup>4</sup>:  $\text{EtHgSnEt}_3$ ,  $\text{n-PrHgSnEt}_3$ ,  $\text{n-BuHgSnEt}_3$ ,  $\text{i-BuHgSnMe}_3$ ,  $\text{i-BuHgSnEt}_3$ ,  $\text{t-BuHgSnBu}_3\text{-i}$ , etc., which decompose on attempted distillation at  $100^{\circ}\text{C}$  and  $10^{-3}$  torr ( $10^{-1}$  Pa), forming Hg metal. The compounds are prone to symmetrization:



The kinetics of the reaction of hexamethylditin with  $\text{Hg(II)}$  chloride or alkylmercury salts are second order. Trialkylstannylmercurials  $\text{R}_3\text{SnHgCl}$  or  $\text{R}_3\text{SnHgR}$  are potential intermediates:



Reactions (h) and (i) are rapid relative to (g)<sup>5,6</sup>.

(A. K. SAWYER)

1. T. N. Mitchell, W. P. Neumann, *J. Organomet. Chem.*, **22**, C25 (1970).
2. T. N. Mitchell, *J. Organomet. Chem.*, **38**, 17 (1972).
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## 5.7.6. Lead-Group-IIB Bonds

### 5.7.6.1. in Alloys and Intermetallics

#### 5.7.6.1.1. from the Elements.

The mutual solubilities of solid Pb and Zn are slight, and according to the binary phase diagram show a eutectic far on the Pb side; no intermetallics exist<sup>1</sup>. Single crystals of the eutectic (1.6 at % Zn) are prepared in a tube of high-melting glass with graphite-coated walls. The components are melted at 500–550°C while the tube is lowered slowly through the heating zone of a vertical furnace<sup>2</sup>. Lead-Zn coatings can be deposited from the gas phase<sup>3</sup>. A eutectic mixture is formed by Pb and Cd (28 at % Cd). The solubility of Pb metal in solid Cd is slight<sup>4</sup>, and only ca. 6 at % Cd are soluble<sup>4,6</sup> in Pb metal at 248°C. Melting the components in a graphite<sup>6</sup> or porcelain crucible<sup>7</sup> is a simple way to produce Pb-Cd alloys. However, the high vapor pressure of Cd requires fusion<sup>6,7</sup> of the components under a protective layer of LiCl and KCl.

Lead amalgams were known in China<sup>8</sup> in the second century A.D. Liquid<sup>9</sup> (e.g., 3 wt % Pb) and solid Pb amalgams are formed by heating Pb and Hg metals in closed Fe crucibles or glass ampules<sup>10</sup>.

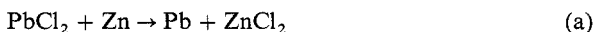
A compound Pb<sub>2</sub>Hg is formed by a peritectic reaction<sup>11</sup> at 145°C.

(F. HUBER, K. GRÄTZ)

1. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958, p. 1118.
2. W. Hofmann, A. Luis, *Metallkd.*, 55, 101 (1964).
3. G. Venturello, S. Allaria, *Metall. Ital.*, 36, 157 (1944).
4. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958, p. 433.
5. L. N. Lankov, Yu. F. Yurchenko, *Ukr. Fiz. Zh.*, 9, 1345 (1964); *Chem. Abstr.*, 62, 10,159 (1965).
6. G. Rienäcker, G. Techel, *Z. Anorg. Allg. Chem.*, 304, 58 (1960).
7. J. Goebel, *Z. Metallkd.*, 14, 357 (1922).
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10. G. Jangg, H. Bach, in *Handbuch der Technischen Elektrochemie*, 2nd ed., G. Eger, ed., Vol. 1, Akademische Verlagsgesellschaft, Leipzig, 1961, p. 592.
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#### 5.7.6.1.2. by Reduction.

Lead-Zn alloys with ≤ 2.5% Pb, which do not segregate, are prepared by mixing solid PbCl<sub>2</sub> and liq Zn at 500–550°C;



PbCl<sub>2</sub> is reduced quantitatively, and ZnCl<sub>2</sub> evaporates<sup>1</sup>.

## 5.7.6. Lead-Group-IIB Bonds

### 5.7.6.1. In Alloys and Intermetallics

#### 5.7.6.1.1. from the Elements.

The mutual solubilities of solid Pb and Zn are slight, and according to the binary phase diagram show a eutectic far on the Pb side; no intermetallics exist<sup>1</sup>. Single crystals of the eutectic (1.6 at % Zn) are prepared in a tube of high-melting glass with graphite-coated walls. The components are melted at 500–550°C while the tube is lowered slowly through the heating zone of a vertical furnace<sup>2</sup>. Lead-Zn coatings can be deposited from the gas phase<sup>3</sup>. A eutectic mixture is formed by Pb and Cd (28 at % Cd). The solubility of Pb metal in solid Cd is slight<sup>4</sup>, and only ca. 6 at % Cd are soluble<sup>4,6</sup> in Pb metal at 248°C. Melting the components in a graphite<sup>6</sup> or porcelain crucible<sup>7</sup> is a simple way to produce Pb-Cd alloys. However, the high vapor pressure of Cd requires fusion<sup>6,7</sup> of the components under a protective layer of LiCl and KCl.

Lead amalgams were known in China<sup>8</sup> in the second century A.D. Liquid<sup>9</sup> (e.g., 3 wt % Pb) and solid Pb amalgams are formed by heating Pb and Hg metals in closed Fe crucibles or glass ampules<sup>10</sup>.

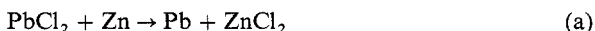
A compound Pb<sub>2</sub>Hg is formed by a peritectic reaction<sup>11</sup> at 145°C.

(F. HUBER, K. GRÄTZ)

1. M. Hansen, K. Anderko, *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, 1958, p. 1118.
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6. G. Rienäcker, G. Techel, *Z. Anorg. Allg. Chem.*, 304, 58 (1960).
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### 5.7.6.1.3. by Electrolysis.

Electrolytic formation of Pb-Zn coatings is described<sup>1</sup>.

Lead-Cd alloys can be separated by electrolysis of melts of  $\text{PbCl}_2$  and  $\text{CdCl}_2$  at a Zn cathode at 510–540°C. The composition corresponds at high current densities to the ratio of the components in the melt<sup>2</sup>. Lead-Cd alloys are also electrodeposited in molten form on small wires from anhyd  $\text{PbBr}_2$ ,  $\text{CdBr}_2$  and  $\text{NH}_4\text{Cl}$  in glycerine at 140°C using high current densities<sup>3</sup>. To produce an alloy with ca. 20 wt % Cd a solution of 9 %  $\text{NH}_4\text{Cl}$ , 1 %  $\text{PbBr}_2$  and 0.3 %  $\text{CdBr}_2$  (wt %) is applied<sup>3</sup>.

Lead can be separated like other metals more noble than Mn from Pb salts in aq acid at Hg cathodes producing Pb amalgams<sup>4,5</sup>.

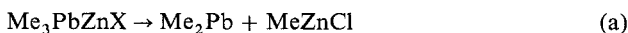
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### 5.7.6.2. in Organolead-Group-IIB Compounds.

Organolead compounds with Pb-group-IIB bonds are unknown (see, e.g., ref. 1). Species with Pb-Zn and Pb-Hg bonds are intermediates, although proof of their formation or even composition is lacking.

The Pb-Zn-bonded intermediates  $\text{Me}_3\text{PbZnCl}$  and  $\text{Me}_2\text{Pb}(\text{Cl})\text{ZnCl}$  explain the reaction<sup>2</sup> of  $\text{R}_3\text{PbCl}$  and  $\text{Me}_2\text{PbCl}_2$  with Zn metal in  $\text{H}_2\text{O}$ . Analogous compounds with Sn-Zn bonds, e.g.,  $\text{Ph}_3\text{SnZnCl}$  are known<sup>3</sup>. The reaction proceeds in two stages, the first being the rapid removal of  $\text{Me}_3\text{PbCl}$  and  $\text{Me}_2\text{PbCl}_2$  from solution and formation of the Pb-Zn intermediates. The slower second step starts with a 1,2-shift of methyl groups from Pb to Zn:



or by:



The resulting species decompose to give the final products<sup>2</sup>,  $\text{CH}_4$ , Pb, ZnO and  $\text{ZnCl}_2$ .

5.7. Formation of Bonds between Elements of Groups IVB and IIB 365  
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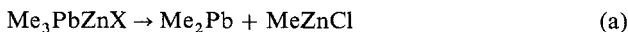
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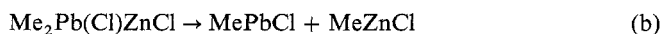
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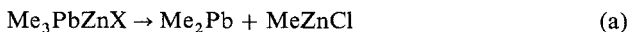
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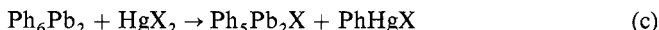


or by:

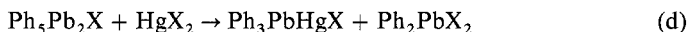


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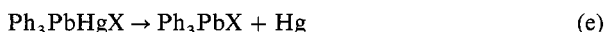
The Pb—Hg species,  $\text{Ph}_3\text{PbHgX}$  ( $\text{X} = \text{Cl}, \text{CH}_3\text{COO}$ )<sup>4</sup>, is an intermediate in the reaction of  $\text{Ph}_6\text{Pb}_2$  and  $\text{HgX}_2$ . The initial and rate-controlling step:



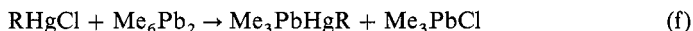
is followed by several fast steps. One subsequent pathway involves further Pb—C cleavage followed by decomposition, while another involves Pb—Pb cleavage, producing the Pb—Hg intermediate  $\text{Ph}_3\text{PbHgX}$ :



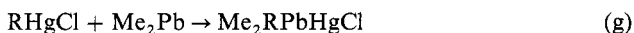
The decomposition of the unstable  $\text{Ph}_3\text{PbHgX}$  is formulated:



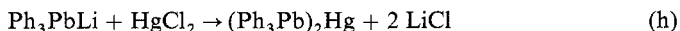
Lead-Hg intermediates also appear in the reaction of  $\text{Me}_6\text{Pb}_2$  and  $\text{RHgCl}$ , resulting in complex stoichiometry<sup>5</sup> with  $\text{Me}_4\text{Pb}$ ,  $\text{Me}_2\text{Hg}$ ,  $\text{PbCl}_2$  and  $\text{Hg}$ . Lead-lead cleavage when  $\text{RHgCl}$  reacts with  $\text{Me}_6\text{Pb}_2$  gives  $\text{Me}_3\text{PbHgR}$ :



whereas reaction with transient  $\text{Me}_2\text{Pb}$  gives  $\text{RMe}_2\text{PbHgCl}$ :



The attempted preparation<sup>6</sup> of  $(\text{Ph}_3\text{Pb})_2\text{Hg}$  by treating an  $\text{Et}_2\text{O}$  suspension of  $\text{Ph}_3\text{PbLi}$  with  $\text{HgCl}_2$  in  $\text{Et}_2\text{O}$  at  $-10^\circ\text{C}$ :



does not work<sup>7</sup>.

(F. HUBER, K. GRÄTZ)

1. T. N. Mitchell, *J. Organomet. Chem.*, **71**, 27 (1974).
2. M. H. Hitchen, A. K. Holliday, R. J. Puddephatt, *J. Organomet. Chem.*, **172**, 427 (1979).
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6. G. Deganello, G. Carturan, P. Uguagliati, *J. Organomet. Chem.*, **17**, 179 (1969).
7. G. Deganello, G. Carturan, P. Uguagliati, *J. Organomet. Chem.*, **18**, 216 (1969).

## Abbreviations

abs	absolute
a.c.	alternating current
Ac	acetyl, $\text{CH}_3\text{CO}$
acac	acetylacetonate anion
acacH	acetylacetone, $\text{CH}_3\text{C(O)CH}_2\text{C(O)CH}_3$
ads	adsorbed
AIBN	2,2'-azobis(isobutyronitrile), $2,2'\text{-}[(\text{CH}_3)_2\text{CCN}]_2\text{N}_2$
Alk	alkyl
am	amine
amt	amount
Am	amyl, $\text{C}_5\text{H}_{11}$
amu	atomic mass unit
anhyd	anhydrous
aq	aqueous
Ar	aryl
asym	asymmetrical, asymmetric
at	atom (not atomic, except in atomic weight)
atm	atmosphere (not atmospheric)
av	average
bcc	body-centered cubic
BD	butadiene
bipy	2,2'-bipyridyl
bipyH	protonated 2,2'-bipyridyl
bp	boiling point
Bu	butyl, $\text{C}_4\text{H}_9$
Bz	benzyl, $\text{C}_6\text{H}_5\text{CH}_2$
ca.	circa, about, approximately
catal	catalyst (not catalyzing, catalysis, catalyzed, etc.)
CDT	cyclododecatriene
Ch.	chapter
COD	cyclooctadiene
conc	concentrated (not concentration)
const.	constant
COT	cyclooctatriene
Cp	cyclopentadienyl, $\text{C}_5\text{H}_5$
CPE	controlled-potential electrolysis
cpm	counts per minute
CT	charge-transfer
CV	cyclic voltammetry
CVD	chemical vapor deposition
CW	continuous wave
d	day, days
DABIP	N,N'-diisopropyl-1,4-diazabutadiene
DBA	dibenzylideneacetone
d.c.	direct current
DDT	dichlorodiphenyltrichloroethane, 1,1,1'-trichloro-2,2-bis-(4-chlorophenyl)ethane
dec	decomposed

DED	1,1-bis(ethoxycarbonyl)ethene-2,2-dithiolate, [[ $(\text{H}_3\text{C}_2\text{OC(O)})_2\text{C}=\text{CS}_2$ ]] <sup>2-</sup>
depe	1,2-bis(diphenylphosphino)ethene, $(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$
diars	1,2-bis(dimethylarsino)benzene, o-phenylenebis(dimethylarsine), $1,2-(\text{CH}_3)_2\text{AsC}_6\text{H}_4\text{As}(\text{CH}_3)_2$
dien	diethylenetriamine, $[\text{H}_2\text{N}(\text{CH}_2)_2]\text{NH}$
diglyme	diethyleneglycol dimethylether, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$
dil	dilute
diop	2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}[\text{OCH}(\text{CH}_3)=\text{CH}_2]\text{CH}[\text{OCH}(\text{CH}_3)=\text{CH}_2]\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$
diphos	1,2-bis(diphenylphosphino)benzene, $1,2-(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$
Div.	division
dme	dropping mercury electrode
DME	1,2-dimethoxyethane, glyme, $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$
DMF	N,N-dimethylformamide, $\text{HC(O)N}(\text{CH}_3)_2$
DMG	dimethylglyoxime, $\text{CH}_3\text{C}(=\text{NOH})\text{C}(=\text{NOH})\text{CH}_3$
DMP	1,2-dimethoxybenzene, 1,2-( $\text{CH}_3\text{O}$ ) $_2\text{C}_6\text{H}_4$
dmpe	1,2-bis(dimethylphosphino)ethane, $(\text{CH}_3)_2\text{P}(\text{CH}_2)_2\text{P}(\text{CH}_3)_2$
DMSO	dimethylsulfoxide, $(\text{CH}_3)_2\text{SO}$
dpam	bis(diphenylarsino)methane, $[(\text{C}_6\text{H}_5)_2\text{As}]_2\text{CH}_2$
dpic	dipicolinate ion
DPP	differential pulse polarography
dppb	1,4-bis(diphenylphosphino)butane, $1,4-(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_4\text{P}(\text{C}_6\text{H}_5)_2$
dppe	1,2-bis(diphenylphosphino)ethane, $1,2-(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$
dppm	bis(diphenylphosphino)methane, $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CH}_2$
dppp	1,3-bis(diphenylphosphino)propane, $1,3-(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2$
dptpe	1,2-bis(di-p-tolylphosphino)ethane, $1,2-(4-\text{CH}_3\text{C}_6\text{H}_4)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_4\text{CH}_3-4)_2$
DTA	differential thermal analysis
DTBQ	3,5-di-t-butyl-o-benzoquinone
DTH	1,6-dithiahexane, butane-1,4-dithiol, $1,4-\text{HS}(\text{CH}_2)_4\text{SH}$
DTS	dithiosquarate
ed.	edition, editor
eds.	editors
EDTA	ethylenediaminetetraacetic acid, $[\text{HOC(O)}]_2\text{N}(\text{CH}_2)_2\text{N}[\text{C(O)OH}]_2$
e.g.	exempli gratia, for example
emf	electromotive force
en	ethylenediamine, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$
enH	protonated ethylenediamine
EPR	electron paramagnetic resonance
equimol	equimolar
equiv	equivalent
EPR	electron paramagnetic resonance
Eq.	equation
ERF	effective reduction factor
ES	excited state
ESR	electron-spin resonance
esu	electrostatic unit
Et	ethyl, $\text{CH}_2\text{CH}_3$
etc.	et cetera, and so forth



Et <sub>2</sub> O	diethyl ether, (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
EtOH	ethanol, C <sub>2</sub> H <sub>5</sub> OH
et seq.	et sequentes, and the following
eu	entropy unit
fac	facial
fcc	face-centered cubic
ff.	following
Fig.	figure
Fl	fluorenyl
fp	freezing point
g	gas
g-at	gram-atom
glyme	1,2-dimethoxyethane, CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>
graph	graphite
GS	ground state
h	hour, hours
Hex	hexyl
hmde	hanging mercury drop electrode
HMPA	hexamethylphosphoramide, [(CH <sub>3</sub> ) <sub>2</sub> N] <sub>3</sub> PO
HOMO	highest occupied molecular orbital
i.e.	id est, that is
Im	imidazole
inter alia	among other things
IR	infrared
irrev	irreversible
ISC	intersystem crossing
isn	isonicotinamide
l	liquid
L	ligand
LC	ligand centered
LF	ligand field
LFER	linear free-energy relationship
liq	liquid
LMCT	ligand-to-metal charge transfer
Ln	lanthanides, rare earths
LSV	linear-scan voltammetry
LUMO	lowest unoccupied molecular orbital
m	meta
max	maximum
M	metal
MC	metal centered
Me	methyl, CH <sub>3</sub>
Men	menthyl
MeOH	methanol, CH <sub>3</sub> OH
mer	meridional; the repeating unit of an oligomer or polymer
mhp	2-hydroxy-6-methylpyridine, 2-HO, 6-CH <sub>3</sub> C <sub>5</sub> H <sub>3</sub> N
min	minimum, minute, minutes
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
mol	molar
mp	melting point
MV	methyl viologen, 1,1'-dimethyl-4,4'-bipyridinium dichloride
n.a.	not available

napy	naphthyridine
NBD	norbornadiene, [2.2.1]bicyclohepta-2,5-diene
neg	negative
nhe	normal hydrogen electrode
NMR	nuclear magnetic resonance
No.	number
np	tris-[2-(diphenylphosphino)ethyl]amine, $N[CH_2CH_2P(C_6H_5)_2]_3$
Np	naphthyl
NPP	normal pulse polarography
NQR	nuclear quadrupole resonance
NTA	nitrilotriacetate
o	ortho
obs	observed
Oct	octyl
OF	oxidation factor
O <sub>h</sub>	octahedral
Oq	oxyquinolate
p	para
p.	page
P	pressure
Pat.	patent
pet.	petroleum
Ph	phenyl, $C_6H_5$
phen	1,10-phenanthroline
Ph <sub>2</sub> PPy	2-(diphenylphosphino)pyridine, $2-(C_6H_5)_2PC_5H_4N$
pip	piperidine, $C_5H_{10}N$
PMDT	pentamethyldiethylenetriamine, $(CH_3)_2N(CH_2)_2N(CH_3)(CH_2)_2N(CH_3)_2$
PMR	proton magnetic resonance
pn	propylene-1,3-diamine, $1,3-H_2NCH_2CH_2CH_2NH_2$
pos	positive
pp.	pages
ppb	parts per billion
ppm	parts per million
ppn	bis(diphenylphosphino)amine, $[(C_6H_5)_2P]_2NH$
ppt	precipitate
Pr	propyl, $C_3H_7$
PSS	photostationary state
PVC	poly(vinyl chloride)
PY	pyridine, $C_5H_5N$
pyr	pyrazine
PZE	potential of zero charge
rac	racemic mixture, racemate
R	organic group; universal gas constant
RDE	rotated disk electrode
RE	rare earths, lanthanides
ref.	reference
rev	reversible
rf	radiofrequency
RF	reduction factor
rh	rhombohedral
rms	root mean square
rpm	revolutions per minute

RT	room temperature
s	second, seconds; solid
sce	saturated calomel electrode
SCE	standard calomel electrode
sec	secondary
Sep	sepulcrate, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane
soln	solution
solv	solvated
sp	specific
STP	standard temperature and pressure
subl	sublimes
Suppl.	supplement
sym	symmetrical, symmetric
t	time; tertiary
T	temperature
T <sub>d</sub>	tetrahedral
TCNE	tetracyanoethylene
TEA	tetraethylammonium ion, [(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N] <sup>+</sup>
terpy	2,2'2"-terpyridyl
tetraphos	Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPhCH <sub>2</sub> CH <sub>2</sub> PPhCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>
TGA	thermogravimetric analysis
THF	tetrahydrofuran
THP	tetrahydropyran
THT	tetrahydrothiophene
TLC	thin-layer chromatography
TMED	N,N,N',N'-tetramethylethylenediamine, (CH <sub>3</sub> ) <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>
TMPH	2,2,6,6-tetramethylpiperidine, 2,2,6,6-(CH <sub>3</sub> ) <sub>4</sub> C <sub>5</sub> H <sub>6</sub> N
Tos	tosyl, tolylsulfonyl, 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>
TPA	tetraphenylarsonium ion, [(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sup>+</sup>
triars	bis-[2-(dimethylarsino)phenyl]methylarsine, [2-(CH <sub>3</sub> ) <sub>2</sub> AsC <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> AsCH <sub>3</sub>
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane, [C <sub>6</sub> H <sub>5</sub> ] <sub>2</sub> PCH <sub>2</sub> ] <sub>3</sub> CCH <sub>3</sub>
trien	triethylenetetraamine, H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>
UV	ultraviolet
v	vicinal
Vi	(E)-[2-(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] C=C(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4
viz.	videlical, that is to say, namely
vol., Vol.	volume
VPE	vapor-phase epitaxy
vs.	versus
wk.	week
wt	weight
X	halogen or pseudohalogen
xs	excess
yr.	year
§	section

## Author Index

The entries of this index were derived directly by computer program from the lists of references. The accuracy of the references was the sole responsibility of the authors. No editorial check, except for format and journal-title abbreviation, was applied. Consequently, errors occurring in authors' names in the references will recur in this index.

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## Compound Index

This index lists individual, fully specified compositions of matter that are mentioned in the text. It is an index of empirical formulas, ordered according to the following system: the elements within a given formula occur in alphabetical sequence except for C, or C and H if present, which always come first. The formulas are ordered alphanumerically without exception.

The index is augmented by successively permuted versions of all empirical formulas. As an example,  $C_3H_3AlO_9$  will appear as such and, at the appropriate positions in the alphanumeric sequence, as  $H_3AlO_9 * C_3$ ,  $AlO_9 * C_3H_3$  and  $O_9 * C_3H_3Al$ . The asterisk identifies a permuted formula and allows the original formula to be reconstructed by shifting to the front the elements that follow the asterisk.

Whenever an empirical formula does not show how the elements are combined in groups, it is followed by a linearized structural formula, which reveals the connectivity of the compound(s) underlying the empirical formula and serves to distinguish substances which are identical in composition but differ in the arrangement of elements.

The nonpermuted empirical formulas are followed by keywords. They describe the context in which the compounds represented by the empirical formulas are discussed. Section numbers direct the reader to relevant positions in the book.

### Ag

#### Ag

Reaction with  $R_3CX$ : 5.6.3

### AgBr

#### AgBr

Reaction with  $RLi$ : 5.6.4

### Ag \* $C_6H_5$

### Ag \* $C_8H_7$

### AgClFe \* $C_{10}H_8$

### AgClP<sub>2</sub>Si<sub>2</sub> \* $C_{17}H_{38}$

### AgClP<sub>3</sub> \* $C_{54}H_{45}$

### AgCl<sub>3</sub>P<sub>3</sub>Sn \* $C_{54}H_{45}$

### AgCuMnO<sub>6</sub> \* $C_{16}H_8$

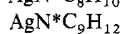
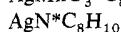
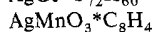
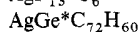
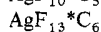
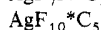
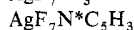
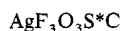
### AgF

#### AgF

Reactions with alkenes: 5.6.4.5

Reactions with alkynes: 5.6.4.5

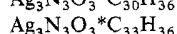
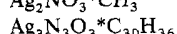
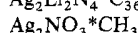
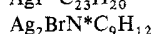
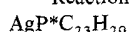
Reactions with allenes: 5.6.4.5



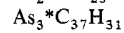
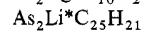
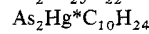
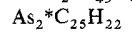
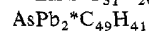
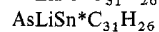
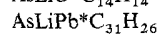
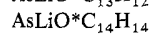
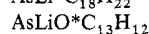
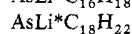
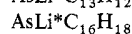
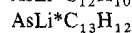
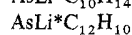
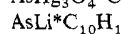
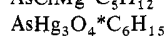
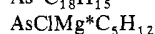
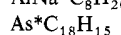
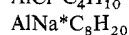
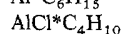
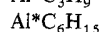
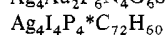
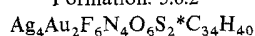
Reaction with Pb—C bonds: 5.6.4

Reaction with RAg: 5.6.4.3

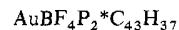
Reaction with alkynes: 5.6.4.3



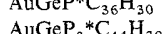
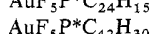
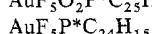
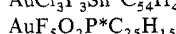
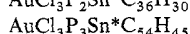
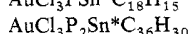
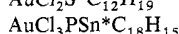
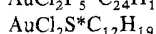
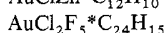
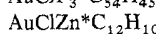
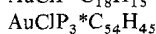
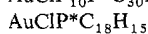
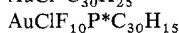
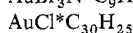
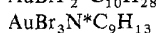
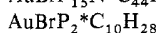
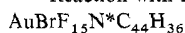
Formation: 5.6.2



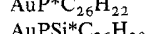
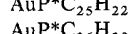
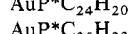
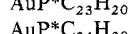
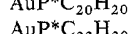
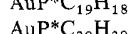
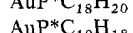
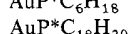
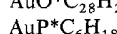
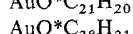
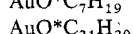
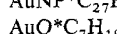
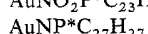
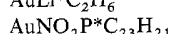
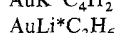
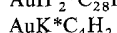
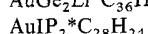
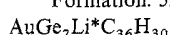
Reaction with  $\text{K}[\text{C}\equiv\text{CH}]$ : 5.6.4.3



Reaction with RLi: 5.6.4



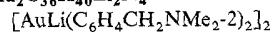
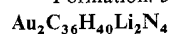
Formation: 5.6.2



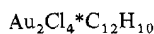
Formation: 5.6.2



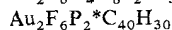
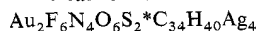
Formation: 5.6.2



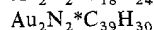
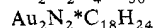
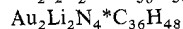
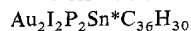
Formation: 5.6.4.1



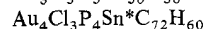
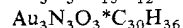
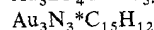
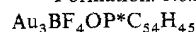
Reaction with ArH: 5.6.4.3



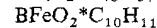
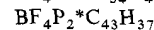
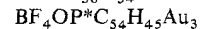
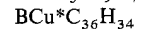
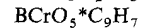
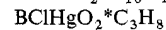
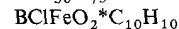
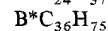
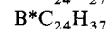
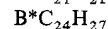
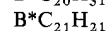
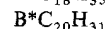
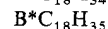
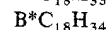
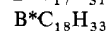
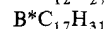
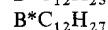
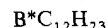
Formation: 5.6.2



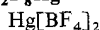
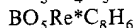
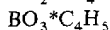
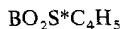
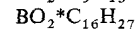
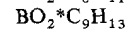
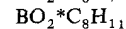
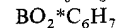
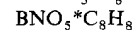
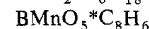
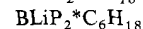
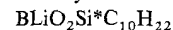
Formation: 5.6.2



Formation: 5.6.2



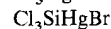
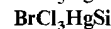
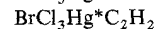
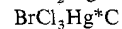
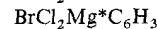
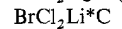
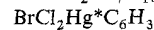
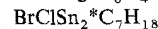
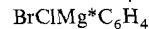
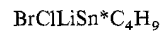
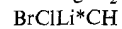
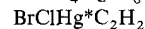
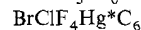
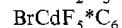
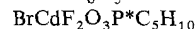
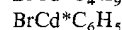
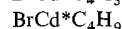
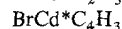
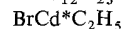
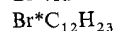
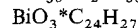
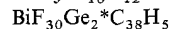
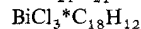
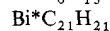
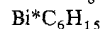
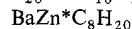
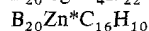
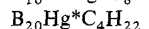
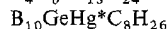
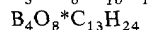
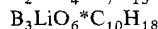
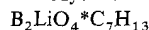
Hydroboration reagent: 5.7.2.3.1



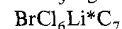
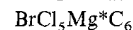
Reaction with alkenes: 5.7.2.3.4



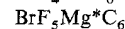
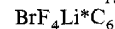
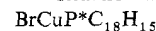
Hydroboration reagent: 5.7.2.3.1



Formation: 5.7.3.3



Reaction with RLi: 5.6.4



$\text{BrF}_5\text{Zn}^*\text{C}_6$   
 $\text{BrF}_6\text{HgO}_2^*\text{C}_6\text{H}_5$   
 $\text{BrF}_{10}\text{Ge}^*\text{C}_{12}\text{H}$   
 $\text{BrF}_{10}\text{Tl}^*\text{C}_{12}$   
 $\text{BrF}_{15}\text{Ge}^*\text{C}_{18}$   
 $\text{BrF}_{15}\text{N}^*\text{C}_{44}\text{H}_{36}\text{Au}$   
 $\text{BrF}_{15}\text{Sn}^*\text{C}_{18}$   
 $\text{BrFeHgO}^*\text{C}_{12}\text{H}_{11}$   
 $\text{BrGe}^*\text{C}_3\text{H}_9$   
 $\text{BrGe}^*\text{C}_6\text{H}_{15}$   
 $\text{BrGe}^*\text{C}_{12}\text{H}_{19}$   
 $\text{BrGe}^*\text{C}_{18}\text{H}_{15}$

**BrGeH<sub>3</sub>**

$\text{H}_3\text{GeBr}$

Reaction with  $(\text{R}_3\text{Ge})_2\text{Hg}$ : 5.7.4, 5.7.4.7

**BrH<sub>3</sub>Si**

$\text{H}_3\text{SiBr}$

Reaction with  $(\text{Me}_3\text{Si})_2\text{Hg}$ : 5.7.3

$\text{BrHg}^*\text{CD}_3$   
 $\text{BrHg}^*\text{CH}_3$   
 $\text{BrHg}^*\text{C}_2\text{H}_3$   
 $\text{BrHg}^*\text{C}_2\text{H}_5$   
 $\text{BrHg}^*\text{C}_3\text{H}_5$   
 $\text{BrHg}^*\text{C}_4\text{H}_9$   
 $\text{BrHg}^*\text{C}_6\text{H}_5$   
 $\text{BrHg}^*\text{C}_7\text{H}_7$   
 $\text{BrHg}^*\text{C}_7\text{H}_{13}$   
 $\text{BrHg}^*\text{C}_8\text{H}_7$   
 $\text{BrHg}^*\text{C}_8\text{H}_9$   
 $\text{BrHg}^*\text{C}_{10}\text{H}_7$   
 $\text{BrHg}^*\text{C}_{14}\text{H}_{11}$   
 $\text{BrHg}^*\text{C}_{16}\text{H}_{15}$   
 $\text{BrHgLiN}^*\text{C}_8\text{H}_9$   
 $\text{BrHgLiN}^*\text{C}_9\text{H}_{11}$   
 $\text{BrHgLiN}^*\text{C}_{14}\text{H}_{13}$   
 $\text{BrHgLiO}^*\text{C}_8\text{H}_8$   
 $\text{BrHgMnO}_3^*\text{C}_6\text{H}_4$   
 $\text{BrHgNO}_2^*\text{C}_6\text{H}_4$   
 $\text{BrHgN}_2^*\text{C}_{15}\text{H}_{17}$   
 $\text{BrHgO}^*\text{C}_7\text{H}_7$   
 $\text{BrHgO}_2^*\text{C}_3\text{H}_9$   
 $\text{BrHgO}_2^*\text{C}_7\text{H}_{15}$   
 $\text{BrHgO}_2^*\text{C}_8\text{H}_7$   
 $\text{BrHgO}_2^*\text{C}_8\text{H}_9$   
 $\text{BrHgO}_2\text{P}_2^*\text{C}_{25}\text{H}_{21}$   
 $\text{BrHgO}_3\text{Re}^*\text{C}_8\text{H}_4$   
 $\text{BrHgP}^*\text{C}_{19}\text{H}_{16}$   
 $\text{BrHgSi}_2^*\text{C}_7\text{H}_{19}$   
 $\text{BrHg}_2\text{O}_2\text{S}^*\text{C}_{10}\text{H}_{11}$   
 $\text{BrLi}^*\text{CH}_2$   
 $\text{BrLi}^*\text{C}_5\text{H}_6$   
 $\text{BrLi}^*\text{C}_5\text{H}_{10}$

$\text{BrLi}^*\text{C}_6\text{H}_4$   
 $\text{BrLi}^*\text{C}_8\text{H}_8$   
 $\text{BrLi}^*\text{C}_{10}\text{H}_6$   
 $\text{BrLi}^*\text{C}_{14}\text{H}_{10}$   
 $\text{BrLiN}^*\text{C}_5\text{H}_3$   
 $\text{BrLiN}^*\text{C}_6\text{H}_{11}$   
 $\text{BrLiN}^*\text{C}_8\text{H}_5$   
 $\text{BrLiO}^*\text{C}_4\text{H}_2$   
 $\text{BrLiO}^*\text{C}_4\text{H}_6$   
 $\text{BrLiO}^*\text{C}_5\text{H}_8$   
 $\text{BrLiO}_2^*\text{C}_{10}\text{H}_{12}$   
 $\text{BrLiO}_2\text{S}^*\text{C}_{12}\text{H}_8$   
 $\text{BrLiS}^*\text{C}_4\text{H}_2$   
 $\text{BrLiSi}_2^*\text{C}_7\text{H}_{18}$   
 $\text{BrLi}_2^*\text{CH}_3$   
 $\text{BrMg}^*\text{CH}_2\text{D}$   
 $\text{BrMg}^*\text{CH}_3$   
 $\text{BrMg}^*\text{C}_2\text{H}_3$   
 $\text{BrMg}^*\text{C}_2\text{H}_5$   
 $\text{BrMg}^*\text{C}_3\text{H}_3$   
 $\text{BrMg}^*\text{C}_3\text{H}_5$   
 $\text{BrMg}^*\text{C}_3\text{H}_7$   
 $\text{BrMg}^*\text{C}_4\text{H}_3$   
 $\text{BrMg}^*\text{C}_4\text{H}_7$   
 $\text{BrMg}^*\text{C}_4\text{H}_9$   
 $\text{BrMg}^*\text{C}_5\text{H}_{11}$   
 $\text{BrMg}^*\text{C}_6\text{D}_5$   
 $\text{BrMg}^*\text{C}_6\text{H}_5$   
 $\text{BrMg}^*\text{C}_6\text{H}_{11}$   
 $\text{BrMg}^*\text{C}_7\text{H}_7$   
 $\text{BrMg}^*\text{C}_8\text{H}_{17}$   
 $\text{BrMgO}^*\text{C}_9\text{H}_9$   
 $\text{BrMgO}_2^*\text{C}_8\text{H}_9$   
 $\text{BrN}^*\text{C}_9\text{H}_{12}\text{Ag}_2$   
 $\text{BrNOZn}^*\text{C}_6\text{H}_{12}$   
 $\text{BrP}_2^*\text{C}_{10}\text{H}_{28}\text{Au}$   
 $\text{BrPb}^*\text{C}_3\text{H}_9$   
 $\text{BrSb}^*\text{C}_{24}\text{H}_{20}$   
 $\text{BrSi}^*\text{C}_3\text{H}_9$   
 $\text{BrSi}^*\text{C}_{12}\text{H}_{27}$   
 $\text{BrSn}^*\text{C}_3\text{H}_9$   
 $\text{BrSn}^*\text{C}_6\text{H}_{15}$   
 $\text{BrSn}^*\text{C}_{18}\text{H}_{15}$   
 $\text{BrSn}^*\text{C}_{21}\text{H}_{21}$   
 $\text{BrZn}^*\text{C}_3\text{H}_3$   
 $\text{BrZn}^*\text{C}_3\text{H}_5$   
 $\text{BrZn}^*\text{C}_6\text{H}_5$   
 $\text{BrZn}^*\text{C}_6\text{H}_{11}$   
 $\text{BrZn}^*\text{C}_7\text{H}_7$

**Br<sub>2</sub>Cd**

$\text{CdBr}_2$

Electrolyte: 5.7.6.1.3

- $\text{Br}_2\text{CuHgP}^*\text{C}_{19}\text{H}_{16}$   
 $\text{Br}_2\text{Cu}_4\text{N}_2^*\text{C}_{36}\text{H}_{40}$   
 $\text{Br}_2\text{Cu}_6\text{N}_4^*\text{C}_{32}\text{H}_{40}$   
 $\text{Br}_2\text{FLi}^*\text{C}$   
 $\text{Br}_2\text{F}_4\text{Hg}_2^*\text{C}_6$   
 $\text{Br}_2\text{F}_8\text{Hg}^*\text{C}_{12}$   
 $\text{Br}_2\text{F}_{20}\text{Ge}_2^*\text{C}_{24}$   
 $\text{Br}_2\text{Ge}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Br}_2\text{Ge}_2^*\text{C}_{24}\text{H}_{20}$   
 $\text{Br}_2\text{Hg}$   
 $\text{HgBr}_2$   
 Reaction with  $\text{RSO}_2\text{M}$ : 5.7.2.3.7  
 Reaction with  $\text{RCu}$ : 5.7.2.3.1  
 Reaction with  $\text{RMgX}$ : 5.7.2.3.1  
 Reaction with  $\text{R}_2\text{CN}_2$ : 5.7.2.3.5  
 Reaction with  $\text{RB(OR')}_2$ : 5.7.2.3.7  
 Reaction with arylazocarboxylates:  
 5.7.2.3.6  
 $\text{Br}_2\text{Hg}_2^*\text{C}_3\text{H}_6$   
 $\text{Br}_2\text{Hg}_2^*\text{C}_5\text{H}_{10}$   
 $\text{Br}_2\text{Hg}_2\text{N}^*\text{C}_{12}\text{H}_{15}$   
 $\text{Br}_2\text{Hg}_2\text{O}^*\text{C}_6\text{H}_{12}$   
 $\text{Br}_2\text{Li}^*\text{CH}$   
 $\text{Br}_2\text{Li}^*\text{C}_5\text{H}_9$   
 $\text{Br}_2\text{Li}^*\text{C}_7\text{H}_5$   
 $\text{Br}_2\text{LiSi}^*\text{C}_4\text{H}_9$   
 $\text{Br}_2\text{LiSn}^*\text{C}_4\text{H}_9$   
 $\text{Br}_2\text{Mg}_2^*\text{C}_5\text{H}_{10}$   
 $\text{Br}_2\text{Na}^*\text{CH}$   
 $\text{Br}_2\text{Pb}$   
 $\text{PbBr}_2$   
 Electrolyte: 5.7.6.1.3  
 $\text{Br}_2\text{SiZn}_2^*\text{C}_4\text{H}_{10}$   
 $\text{Br}_2\text{Sn}_2^*\text{C}_7\text{H}_{18}$   
 $\text{Br}_2\text{Zn}_2^*\text{C}_4\text{H}_8$   
 $\text{Br}_2\text{Zn}_2^*\text{C}_6\text{H}_{10}$   
 $\text{Br}_3\text{Li}^*\text{C}$   
 $\text{Br}_3\text{N}^*\text{C}_9\text{H}_{13}\text{Au}$   
 $\text{Br}_3\text{Sb}^*\text{C}_{18}\text{H}_{12}$   
 $\text{Br}_4\text{Hg}^*\text{C}_{12}\text{H}_5$   
 $\text{Br}_5\text{HgO}_2^*\text{C}_{13}\text{H}_5$   
 $\text{Br}_5\text{Li}^*\text{C}_6$   
 $\text{Br}_6\text{Hg}^*\text{C}_2$   
 $\text{Br}_6\text{Hg}^*\text{C}_6$   
 $\text{Br}_8\text{Cl}_2\text{Hg}^*\text{C}_{12}$   
 $\text{Br}_8\text{Cl}_2\text{HgO}_4^*\text{C}_{14}$   
 $\text{Br}_8\text{F}_2\text{Hg}^*\text{C}_{12}$   
 $\text{Br}_8\text{F}_2\text{HgO}_4^*\text{C}_{14}$   
 $\text{Br}_8\text{HgO}_2^*\text{C}_{14}\text{H}_6$   
 $\text{Br}_8\text{HgO}_6^*\text{C}_{16}\text{H}_6$   
 $\text{Br}_{10}\text{Hg}^*\text{C}_{12}$   
**C**  
 Reaction with Li metal: 5.5.2.1  
**CAgF<sub>3</sub>O<sub>3</sub>S**  
 $\text{AgO}_3\text{SCF}_3$   
 Reaction with NaR: 5.6.4.1  
**CBrCl<sub>2</sub>Li**  
 $\text{BrCl}_2\text{CLi}$   
 Formation: 5.5.2.3.3  
**CBrCl<sub>3</sub>Hg**  
 $\text{CCl}_3\text{HgBr}$   
 Formation: 5.7.2.2.1  
 Reaction with  $\text{R}_2\text{CN}_2$ : 5.7.2.3.3  
**CBR<sub>2</sub>FLi**  
 $\text{Br}_2\text{FCLi}$   
 Formation: 5.5.2.3.3  
**CBr<sub>3</sub>Li**  
 $\text{Br}_3\text{CLi}$   
 Formation: 5.5.2.3.2, 5.5.2.3.3  
**CCl<sub>2</sub>FLi**  
 $\text{CFCl}_2\text{Li}$   
 Formation: 5.5.2.3.3  
**CCl<sub>3</sub>Li**  
 $\text{Cl}_3\text{CLi}$   
 Formation: 5.5.2.3.2, 5.5.2.3.3  
**CCl<sub>4</sub>**  
 $\text{CCl}_4$   
 Reaction with Li metal: 5.5.2.2.1  
**CCl<sub>4</sub>Hg<sub>4</sub>**  
 $\text{C(HgCl)}_4$   
 Formation: 5.7.2.3.7  
**CCl<sub>7</sub>LiSi<sub>2</sub>**  
 $\text{Cl}_3\text{SiCCl(Li)SiCl}_3$   
 Formation: 5.5.2.3.3  
**CCuF<sub>3</sub>O<sub>3</sub>S**  
 $\text{Cu[O}_3\text{SCF}_3]$   
 Reaction with  $\text{RCu}$ : 5.6.4.1  
**CCuN**  
 $\text{CuCN}$   
 Reaction with  $\text{RCu}$ : 5.6.4.1  
**CCuNS**  
 $\text{CuSCN}$   
 Reaction with  $\text{RCu}$ : 5.6.4.1  
**CD<sub>3</sub>BrHg**  
 $\text{CD}_3\text{HgBr}$   
 Formation: 5.7.2.3.2  
**CD<sub>3</sub>ClHg**  
 $\text{CD}_3\text{HgCl}$   
 Formation: 5.7.2.3.2  
**CD<sub>3</sub>HgI**  
 $\text{CD}_3\text{HgI}$   
 Formation: 5.7.2.3.2  
**CF<sub>3</sub>HgI**  
 $\text{CF}_3\text{HgI}$   
 Formation: 5.7.2.2.1



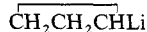
- CHBrCILI**  
 CHBrCILI  
 Formation: 5.5.2.3.3
- CHBr<sub>2</sub>Li**  
 CHBr<sub>2</sub>Li  
 Formation: 5.5.2.3.2
- CHBr<sub>2</sub>Na**  
 Na[CHBr<sub>2</sub>]  
 Formation: 5.5.3.3.1
- CHCl<sub>2</sub>Li**  
 CHCl<sub>2</sub>Li  
 Formation: 5.5.2.3.2, 5.5.2.3.1
- CHCl<sub>3</sub>Hg<sub>3</sub>**  
 HC(HgCl)<sub>3</sub>  
 Formation: 5.7.2.3.7
- CH<sub>2</sub>BrLi**  
 BrH<sub>2</sub>CLi  
 Formation: 5.5.2.3.3
- CH<sub>2</sub>CILi**  
 H<sub>2</sub>ClCLi  
 Formation: 5.5.2.3.3  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- CH<sub>2</sub>Cl<sub>2</sub>Hg<sub>2</sub>**  
 H<sub>2</sub>C(HgCl)<sub>2</sub>  
 Formation: 5.7.2.3.7
- CH<sub>2</sub>DBrMg**  
 DCH<sub>2</sub>MgBr  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- CH<sub>2</sub>HgI<sub>2</sub>**  
 ICH<sub>2</sub>HgI  
 Formation: 5.7.2.2.1
- CH<sub>2</sub>Hg<sub>2</sub>I<sub>2</sub>**  
 CH<sub>2</sub>(HgI)<sub>2</sub>  
 Formation: 5.7.2.2.1  
 Reaction with RLi: 5.5.2.3.1
- CH<sub>2</sub>I<sub>2</sub>Zn**  
 IZnCH<sub>2</sub>I  
 Formation: 5.7.2.2.1, 5.7.2.3.5
- CH<sub>2</sub>I<sub>2</sub>Zn<sub>2</sub>**  
 (IZn)<sub>2</sub>CH<sub>2</sub>  
 Formation: 5.7.2.2.1
- CH<sub>2</sub>Li<sub>2</sub>**  
 CH<sub>2</sub>Li<sub>2</sub>  
 Formation: 5.5.2.2.1
- CH<sub>2</sub>N<sub>2</sub>**  
 CH<sub>2</sub>N<sub>2</sub>  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.5  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.5
- CH<sub>3</sub>Ag<sub>2</sub>NO<sub>3</sub>**  
 AgCH<sub>3</sub> · AgNO<sub>3</sub>  
 Formation: 5.6.4.3
- CH<sub>3</sub>BrHg**  
 CH<sub>3</sub>HgBr  
 Formation: 5.7.2.3.1
- CH<sub>3</sub>BrLi<sub>2</sub>**  
 CH<sub>3</sub>Li · LiBr  
 Reaction with (Me<sub>3</sub>Si)<sub>4</sub>Si: 5.5.4.2.2
- CH<sub>3</sub>BrMg**  
 CH<sub>3</sub>MgBr  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- CH<sub>3</sub>CdCl**  
 CH<sub>3</sub>CdCl  
 Reaction with Ph<sub>3</sub>SnH: 5.7.5.2.2
- CH<sub>3</sub>CdI**  
 CH<sub>3</sub>CdI  
 Formation: 5.7.2.2.1
- CH<sub>3</sub>ClHg**  
 CH<sub>3</sub>HgCl  
 Formation: 5.7.2.3.7
- CH<sub>3</sub>CIOZn**  
 ClZnOCH<sub>3</sub>  
 Formation: 5.7.5.1.1
- CH<sub>3</sub>FHg**  
 CH<sub>3</sub>HgF  
 Formation: 5.7.2.3.2
- CH<sub>3</sub>HgI**  
 CH<sub>3</sub>HgI  
 Formation: 5.7.2.2.1
- CH<sub>3</sub>IMg**  
 CH<sub>3</sub>MgI  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1
- CH<sub>3</sub>K**  
 K[CH<sub>3</sub>]  
 Formation: 5.5.3.2.3, 5.5.3.3.2
- CH<sub>3</sub>KO**  
 K[OCH<sub>3</sub>]  
 Base for metallation reaction: 5.5.3.3.1
- CH<sub>3</sub>Li**  
 CH<sub>3</sub>Li  
 Formation: 5.5.2.2.1, 5.5.2.3.1  
 Reaction with Ph<sub>4</sub>SbBr: 5.5.2.3.1  
 Reaction with RX: 5.5.2.3.3  
 Reaction with disilanes: 5.5.4.2.2  
 Substrate in metal-metal exchange: 5.5.3.3.2
- CH<sub>3</sub>Na**  
 Na[CH<sub>3</sub>]  
 Formation: 5.5.3.2.3
- CH<sub>3</sub>NaO**  
 Na[CH<sub>3</sub>O]  
 Reaction with disilanes: 5.5.4.2.2
- CH<sub>4</sub>Cl<sub>2</sub>Si**  
 (CH<sub>3</sub>)Cl<sub>2</sub>SiH  
 Reaction with R<sub>2</sub>Hg: 5.7.3.3
- CH<sub>5</sub>GeNa**  
 Na[CH<sub>3</sub>GeH<sub>2</sub>]  
 Formation: 5.5.5.4

- CH<sub>5</sub>NaSn**  
Na[CH<sub>3</sub>SnH<sub>2</sub>]  
Formation: 5.5.6.4
- CH<sub>6</sub>Ge**  
CH<sub>3</sub>GeH<sub>3</sub>  
Reaction with Na metal: 5.5.5.4
- CKN**  
KCN  
Reaction with (R<sub>3</sub>Si)<sub>2</sub>Hg: 5.7.3.5
- CK<sub>2</sub>O<sub>3</sub>**  
K<sub>2</sub>CO<sub>3</sub>  
Electrolyte: 5.5.7.1.3
- CLi<sub>4</sub>**  
CLi<sub>4</sub>  
Formation: 5.5.2.2.1
- CNa<sub>2</sub>O<sub>3</sub>**  
Na<sub>2</sub>CO<sub>3</sub>  
Electrolyte: 5.5.7.1.3
- C<sub>2</sub>Br<sub>6</sub>Hg**  
(CBr<sub>3</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.7
- C<sub>2</sub>CdN<sub>2</sub>S<sub>2</sub>**  
Cd[SCN]<sub>2</sub>  
Reaction with RK: 5.7.2.3.1
- C<sub>2</sub>Cl<sub>2</sub>Li<sub>2</sub>O<sub>2</sub>**  
Cl<sub>2</sub>C(Li)CO<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>Zn**  
CF<sub>3</sub>CCl<sub>2</sub>ZnCl  
Formation: 5.7.2.2.1
- C<sub>2</sub>Cl<sub>3</sub>Li**  
CCl<sub>2</sub>=CClLi  
Formation: 5.5.2.3.3
- C<sub>2</sub>Cl<sub>6</sub>Hg**  
(CCl<sub>3</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.7
- C<sub>2</sub>D<sub>6</sub>Hg**  
(CD<sub>3</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.2.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>2</sub>F<sub>2</sub>HgN<sub>4</sub>O<sub>8</sub>**  
Hg[C(NO<sub>2</sub>)<sub>2</sub>F]<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>2</sub>F<sub>3</sub>Li**  
CF<sub>2</sub>=CFLi  
Formation: 5.5.2.3.1, 5.5.2.3.2, 5.5.2.3.3  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>2</sub>F<sub>6</sub>Hg**  
(CF<sub>3</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.2.1, 5.7.2.3.7
- C<sub>2</sub>HCl<sub>2</sub>Li**  
(E)-ClCH=CClLi  
Formation: 5.5.2.3.2
- C<sub>2</sub>HF<sub>2</sub>Li**  
CF<sub>2</sub>=CHLi  
Formation: 5.5.2.3.2
- C<sub>2</sub>HLi**  
HC≡CLi  
Formation: 5.5.2.2.4, 5.5.2.3.2
- C<sub>2</sub>HLi<sub>2</sub>N**  
Li<sub>2</sub>CHCN  
Formation: 5.5.2.3.2
- C<sub>2</sub>HNa**  
Na[HC≡C]  
Formation: 5.5.3.1.1, 5.5.3.2.5, 5.5.3.3.1
- C<sub>2</sub>H<sub>2</sub>BrClHg**  
trans-CHCl=CHHgBr  
Formation: 5.7.2.3.7
- C<sub>2</sub>H<sub>2</sub>BrCl<sub>3</sub>Hg**  
CCl<sub>3</sub>HgCH<sub>2</sub>Br  
Formation: 5.7.2.3.3
- C<sub>2</sub>H<sub>2</sub>ClHgN**  
ClHgCH<sub>2</sub>CN  
Formation: 5.7.2.3.1
- C<sub>2</sub>H<sub>2</sub>ClLi**  
CH<sub>2</sub>=CClLi  
Formation: 5.5.2.3.2  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>Hg**  
cis-CHCl=CHHgCl  
Formation: 5.7.2.3.3, 5.7.2.3.2  
trans-CHCl=CHHgCl  
Formation: 5.7.2.3.3
- C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>HgO**  
ClHgCH<sub>2</sub>COCli  
Formation: 5.7.2.3.3
- C<sub>2</sub>H<sub>2</sub>LiN**  
LiCH<sub>2</sub>CN  
Formation: 5.5.2.3.2  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
LiCH<sub>2</sub>NC  
Formation: 5.5.2.3.2
- C<sub>2</sub>H<sub>2</sub>Li<sub>2</sub>OS**  
LiCH<sub>2</sub>C(O)SLi  
Formation: 5.5.2.3.2
- C<sub>2</sub>H<sub>3</sub>BrHg**  
CH<sub>2</sub>=CHHgBr  
Formation: 5.7.2.3.1
- C<sub>2</sub>H<sub>3</sub>BrMg**  
CH<sub>2</sub>=CHMgBr  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>2</sub>H<sub>3</sub>ClHg**  
CH<sub>2</sub>=CHHgCl  
Formation: 5.7.2.3.1

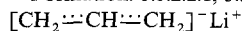
- $C_2H_3Cl_2Li$**   
 $CH_3CCl_2Li$   
 Formation: 5.5.2.3.2
- $C_2H_3Li$**   
 $CH_2=CHLi$   
 Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.3.1, 5.5.2.3.3, 5.5.7.3
- $C_2H_3LiN_4$**   
 $\overline{N}NC(Li)NCH_3$   
 Formation: 5.5.2.3.2
- $C_2H_4CdI_2$**   
 $(ICH_2)_2Cd$   
 Formation: 5.7.2.3.5
- $C_2H_4Cl_2Hg$**   
 $CH_3CHClHgCl$   
 Reaction with  $R_2CN_2$ : 5.7.2.3.3  
 $(ClCH_2)_2Hg$   
 Formation: 5.7.2.3.3
- $C_2H_4Cl_2Zn$**   
 $(ClCH_2)_2Zn$   
 Formation: 5.7.2.3.1, 5.7.2.3.5
- $C_2H_4D_2Zn$**   
 $(DCH_2)_2Zn$   
 Formation: 5.7.2.3.1
- $C_2H_4I_2Zn$**   
 $(ICH_2)_2Zn$   
 Formation: 5.7.2.3.5
- $C_2H_4Li_2$**   
 $CH_3CHLi_2$   
 Formation: 5.5.2.2.2
- $C_2H_4Li_2NO_2$**   
 $[CH_3CHNO_2]^{2-}2Li^+$   
 Formation: 5.5.2.3.2
- $C_2H_5BrCd$**   
 $C_2H_5CdBr$   
 Formation: 5.7.2.3.2
- $C_2H_5BrHg$**   
 $C_2H_5HgBr$   
 Formation: 5.7.2.3.1
- $C_2H_5BrMg$**   
 $C_2H_5MgBr$   
 Reaction with  $HgX_2$ : 5.7.2.3.1
- $C_2H_5CdCl$**   
 $C_2H_5CdCl$   
 Formation: 5.7.2.3.2
- $C_2H_5CdI$**   
 $C_2H_5CdI$   
 Formation: 5.7.2.2.1
- $C_2H_5ClHg$**   
 $C_2H_5HgCl$   
 Formation: 5.7.2.3.2
- Reaction with  $R_3GeGeR_3$ : 5.7.4.5
- $C_2H_5ClHgO$**   
 $HOCH_2CH_2HgCl$   
 Formation: 5.7.2.3.3
- $C_2H_5ClHgO_2$**   
 $CH_2(OOH)CH_2HgCl$   
 Formation: 5.7.2.3.3
- $C_2H_5ClZn$**   
 $C_2H_5ZnCl$   
 Formation: 5.7.2.3.2  
 Reaction with  $ArC\equiv CH$ : 5.7.2.4.1  
 Reaction with  $Ph_3SnH$ : 5.7.5.2.1  
 Reaction with  $R_3SnH$ : 5.7.5.2.1
- $C_2H_5Cl_3HgSi$**   
 $Cl_3SiHgC_2H_5$   
 Formation: 5.7.3.3  
 Reaction with  $HX$ : 5.7.3.3
- $C_2H_5IZn$**   
 $C_2H_5ZnI$   
 Formation: 5.7.2.2.1, 5.7.2.3.2  
 Reaction with  $ArC\equiv CH$ : 5.7.2.4.1
- $C_2H_5KOS$**   
 $K[CH_3S(=O)CH_2]$   
 Formation: 5.5.3.3.1
- $C_2H_5Li$**   
 $CH_3CH_2Li$   
 Formation: 5.5.2.2.1, 5.5.2.2.2  
 Reaction with  $RC\equiv CH$ : 5.5.2.3.2  
 Substrate in metal-metal exchange: 5.5.3.3.2  
 Transmetallation: 5.5.2.3.1
- $C_2H_5LiN_2O$**   
 $O=NN(CH_3)CH_2Li$   
 Formation: 5.5.2.3.2
- $C_2H_5LiO$**   
 $CH_3OCH_2Li$   
 Formation: 5.5.2.2.1, 5.5.2.3.1
- $C_2H_5LiOS$**   
 $CH_3SOCH_2Li$   
 Formation: 5.5.2.3.2
- $C_2H_5LiO_2S$**   
 $CH_3OS(O)CH_2Li$   
 Formation: 5.5.2.3.2
- $C_2H_5LiO_3S$**   
 $CH_3OS(O)_2CH_2Li$   
 Formation: 5.5.2.3.2
- $C_2H_5LiS$**   
 $CH_3SCH_2Li$   
 Formation: 5.5.2.3.1, 5.5.2.3.2
- $C_2H_5Na$**   
 $Na[CH_3CH_2]$   
 Formation: 5.5.3.2.3, 5.5.3.3.2, 5.5.7.3

- C<sub>2</sub>H<sub>6</sub>NaOS**  
Na[CH<sub>3</sub>S(=O)CH<sub>2</sub>]  
Formation: 5.5.3.3.1
- C<sub>2</sub>H<sub>6</sub>AuLi**  
AuLi(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.6.4.3
- C<sub>2</sub>H<sub>6</sub>Cd**  
(CH<sub>3</sub>)<sub>2</sub>Cd  
Formation: 5.7.2.3.1  
Reaction with CdX<sub>2</sub>: 5.7.2.3.2  
Reaction with (CH<sub>2</sub>=CH)<sub>2</sub>Hg: 5.7.2.4.3  
Reaction with Ph<sub>3</sub>SnH: 5.7.5.2.2
- C<sub>2</sub>H<sub>6</sub>Cl<sub>2</sub>Pb**  
(CH<sub>3</sub>)<sub>2</sub>PbCl<sub>2</sub>  
Reaction with Zn metal: 5.7.6.2
- C<sub>2</sub>H<sub>6</sub>Cl<sub>4</sub>HgSi<sub>2</sub>**  
(CH<sub>3</sub>Cl<sub>2</sub>Si)<sub>2</sub>Hg  
Formation: 5.7.3.3  
<sup>1</sup>H-NMR: 5.7.3  
Reaction with (R<sub>3</sub>Si)<sub>2</sub>Hg: 5.7.3.5
- C<sub>2</sub>H<sub>6</sub>CuLi**  
CuLi(CH<sub>3</sub>)<sub>2</sub>  
Reaction with ArH: 5.6.4.3
- C<sub>2</sub>H<sub>6</sub>Hg**  
(CH<sub>3</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.7  
Reaction with Hg<sub>2</sub>X<sub>2</sub>: 5.7.2.3.2  
Reaction with Zn metal: 5.7.2.2.2  
Reaction with Na, K or Na-K: 5.5.3.2.3  
Transmetallation: 5.5.2.3.1
- C<sub>2</sub>H<sub>6</sub>HgSi**  
HgSi(CH<sub>3</sub>)<sub>2</sub>  
Formation and decomposition: 5.7.3.2
- C<sub>2</sub>H<sub>6</sub>Hg<sub>2</sub>O**  
(CH<sub>3</sub>Hg)<sub>2</sub>O  
Reaction with aliphatics: 5.7.2.3.4
- C<sub>2</sub>H<sub>6</sub>Na<sub>2</sub>Sn**  
Na<sub>2</sub>[(CH<sub>3</sub>)<sub>2</sub>Sn]  
Formation: 5.5.6.2.2, 5.5.6.4
- C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>Zn**  
Zn(OCH<sub>3</sub>)<sub>2</sub>  
Formation: 5.7.5.1.1
- C<sub>2</sub>H<sub>6</sub>Sn**  
(CH<sub>3</sub>)<sub>2</sub>Sn  
Formation: 5.5.6.2.1, 5.5.6.3.1  
Reaction with RLi: 5.5.6.2.1
- C<sub>2</sub>H<sub>6</sub>Zn**  
(CH<sub>3</sub>)<sub>2</sub>Zn  
Formation: 5.7.2.2.1, 5.7.2.2.2  
Reaction with R<sub>3</sub>B: 5.7.2.4.3
- C<sub>2</sub>H<sub>7</sub>ClSi**  
(CH<sub>3</sub>)<sub>2</sub>ClSiH  
Reaction with R<sub>2</sub>Hg: 5.7.3.3
- C<sub>2</sub>H<sub>7</sub>GeLi**  
C<sub>2</sub>H<sub>5</sub>GeH<sub>2</sub>Li  
Formation: 5.5.5.4
- C<sub>2</sub>H<sub>7</sub>GeNa**  
Na[C<sub>2</sub>H<sub>5</sub>GeH<sub>2</sub>]  
Formation: 5.5.5.4
- C<sub>2</sub>H<sub>7</sub>NaSn**  
Na[(CH<sub>3</sub>)<sub>2</sub>SnH]  
Formation: 5.5.6.4
- C<sub>2</sub>H<sub>8</sub>Ge**  
C<sub>2</sub>H<sub>5</sub>GeH<sub>3</sub>  
Reaction with Li metal: 5.5.5.4  
Reaction with Na metal: 5.5.5.4
- C<sub>2</sub>HgN<sub>2</sub>**  
Hg(CN)<sub>2</sub>  
Reaction with R<sub>2</sub>Hg: 5.7.2.3.2
- C<sub>2</sub>HgN<sub>2</sub>O<sub>2</sub>**  
Hg(CNO)<sub>2</sub>  
Reaction with RMgX: 5.7.2.3.1
- C<sub>2</sub>HgN<sub>6</sub>O<sub>12</sub>**  
Hg[C(NO<sub>2</sub>)<sub>3</sub>]<sub>2</sub>  
Formation: 5.7.2.3.4  
Reaction with alkenes: 5.7.2.3.3
- C<sub>2</sub>Li<sub>2</sub>**  
LiC≡CLi  
Formation: 5.5.2.3.2, 5.5.2.1
- C<sub>2</sub>Li<sub>6</sub>**  
Li<sub>3</sub>CC≡Li<sub>3</sub>  
Formation: 5.5.2.2.2
- C<sub>2</sub>Na<sub>2</sub>**  
NaC≡CNa  
Formation: 5.5.3.1.1
- C<sub>3</sub>AgF<sub>5</sub>**  
AgC(CF<sub>3</sub>)=CF<sub>2</sub>  
Formation: 5.6.4.5
- C<sub>3</sub>AgF<sub>7</sub>**  
AgCF(CF<sub>3</sub>)<sub>2</sub>  
Reaction with RBr: 5.6.4.2
- C<sub>3</sub>Cl<sub>2</sub>Hg<sub>2</sub>N<sub>2</sub>**  
(ClHg)<sub>2</sub>C(CN)<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>3</sub>F<sub>6</sub>**  
CF<sub>3</sub>CF=CF<sub>2</sub>  
Reaction with AgF: 5.6.4
- C<sub>3</sub>F<sub>7</sub>IZn**  
C<sub>3</sub>F<sub>7</sub>ZnI  
Formation: 5.7.2.2.1
- C<sub>3</sub>F<sub>7</sub>Li**  
C<sub>3</sub>F<sub>7</sub>Li  
Formation: 5.5.2.3.3
- C<sub>3</sub>HILiNS**  
SN=CHCl=CLi  
Formation: 5.5.2.3.2

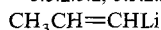
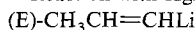
- C<sub>3</sub>HLi<sub>3</sub>**  
 $\text{Li}_2\text{CHC}\equiv\text{CLi}$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>2</sub>ClHgNS**  
 $\text{CHCHN}=\text{C}(\text{HgCl})\text{S}$   
 Formation: 5.7.2.3.6
- C<sub>3</sub>H<sub>2</sub>CuNO<sub>2</sub>**  
 $\text{CuO}_2\text{CCH}_2\text{CN}$   
 Decarboxylation: 5.6.4.5
- C<sub>3</sub>H<sub>2</sub>F<sub>3</sub>Li**  
 $\text{CH}_2=\text{C}(\text{CF}_3)\text{Li}$   
 Formation: 5.5.2.3.3
- C<sub>3</sub>H<sub>2</sub>LiNS**  
 $\text{SCH}=\text{CHN}=\text{CLi}$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>2</sub>Li<sub>2</sub>**  
 $\text{LiCH}_2\text{C}\equiv\text{CLi}$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>3</sub>BrMg**  
 $\text{HC}\equiv\text{CCH}_2\text{MgBr}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- C<sub>3</sub>H<sub>3</sub>BrZn**  
 $\text{HC}\equiv\text{CCH}_2\text{ZnBr}$   
 Formation: 5.7.2.2.1
- C<sub>3</sub>H<sub>3</sub>ClHg**  
 $\text{ClHgCH}=\text{C}=\text{CH}_2$   
 Formation: 5.7.2.3.1
- C<sub>3</sub>H<sub>3</sub>Cl<sub>2</sub>Li**  
 $\text{CCl}_2=\text{CHCH}_2\text{Li}$   
 Formation: 5.5.2.3.1, 5.5.2.3.2  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>3</sub>H<sub>3</sub>Cl<sub>3</sub>Hg**  
 $\text{CCl}_2=\text{CHCH}_2\text{HgCl}$   
 Formation: 5.7.2.3.1
- C<sub>3</sub>H<sub>3</sub>D<sub>2</sub>HgN**  
 $\text{CH}_3\text{HgCD}_2\text{CN}$   
 Formation: 5.7.2.3.4
- C<sub>3</sub>H<sub>3</sub>F<sub>2</sub>Li**  
 $[\text{CF}_2\cdots\text{CH}\cdots\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>3</sub>H<sub>3</sub>Li**  
 $\text{CH}_2=\text{C}=\text{CHLi}$   
 Formation: 5.5.2.3.2  
 $\text{CH}_3\text{C}\equiv\text{CLi}$   
 Formation: 5.5.2.2.4, 5.5.2.3.2
- C<sub>3</sub>H<sub>3</sub>LiN<sub>2</sub>O**  
 $\text{CH}_3\text{COC}(\text{Li})\text{N}_2$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>3</sub>ClLi**  
 $[\text{CHCl}\cdots\text{CH}\cdots\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.1
- C<sub>3</sub>H<sub>4</sub>Cl<sub>2</sub>Hg**  
 $(\text{E})\text{-CH}_3\text{CCl}=\text{CHHgCl}$   
 Formation: 5.7.2.3.3
- C<sub>3</sub>H<sub>4</sub>KLiO**  
 $\text{K}[\text{LiCH}_2\text{C}(\text{O})\text{CH}_2]$   
 Formation: 5.5.3.3.1
- C<sub>3</sub>H<sub>4</sub>LiN**  
 $\text{CH}_3\text{CHLiNC}$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>4</sub>Li<sub>2</sub>NO<sub>2</sub>**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CHNO}_2]^{2-} 2\text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>4</sub>Li<sub>2</sub>O**  
 $\text{LiCH}=\text{CHCH}_2\text{OLi}$   
 Formation: 5.5.2.3.1
- C<sub>3</sub>H<sub>4</sub>Li<sub>2</sub>O<sub>2</sub>**  
 $(\text{CH}_3)\text{HC}(\text{Li})\text{CO}_2\text{Li}$   
 Formation: 5.5.2.3.5
- C<sub>3</sub>H<sub>4</sub>Li<sub>2</sub>S**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CHSLi}] \text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>5</sub>BrHg**  
 $\text{cis-CH}_3\text{CH}=\text{CHHgBr}$   
 Formation: 5.7.2.3.2  
 $\text{trans-CH}_3\text{CH}=\text{CHHgBr}$   
 Formation: 5.7.2.3.2
- C<sub>3</sub>H<sub>5</sub>BrMg**  
 $\text{CH}_2=\text{CHCH}_2\text{MgBr}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1  
 $\text{cyclo-C}_3\text{H}_5\text{MgBr}$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1  
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- C<sub>3</sub>H<sub>5</sub>BrZn**  
 $\text{CH}_2=\text{CHCH}_2\text{ZnBr}$   
 Reaction with  $\text{ArC}\equiv\text{CH}$ : 5.7.2.4.1  
 Self-condensation: 5.7.2.4.2
- C<sub>3</sub>H<sub>5</sub>ClHg**  
 $\text{CH}_2\text{CH}_2\text{CHHgCl}$   
 Formation: 5.7.2.3.1  
 $\text{CH}_3\text{CH}=\text{CHHgCl}$   
 Formation: 5.7.2.3.1
- C<sub>3</sub>H<sub>5</sub>ClHgO**  
 $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{HgCl}$   
 Reaction with  $\text{R}_2\text{CN}_2$ : 5.7.2.3.3
- C<sub>3</sub>H<sub>5</sub>Cs**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CH}_2]^- \text{Cs}^+$   
 Formation: 5.5.3.2.3, 5.5.3.2.6
- C<sub>3</sub>H<sub>5</sub>HgIO**  
 $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{HgI}$   
 Formation: 5.7.2.3.4
- C<sub>3</sub>H<sub>5</sub>HgN**  
 $\text{CH}_3\text{HgCH}_2\text{CN}$   
 Formation: 5.7.2.3.4
- C<sub>3</sub>H<sub>5</sub>K**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CH}_2]^- \text{K}^+$   
 Formation: 5.5.3.2.2, 5.5.3.2.3, 5.5.3.2.5, 5.5.3.3.1

**C<sub>3</sub>H<sub>5</sub>Li**

Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.3.1

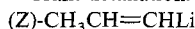


Formation: 5.5.2.2.5, 5.5.3.2.5, 5.5.2.3.1, 5.5.2.3.2, 5.5.2.3.4

Reaction with HgX<sub>2</sub>: 5.7.2.3.1

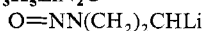
Formation: 5.5.2.2.1, 5.5.2.3.3, 5.5.3.2.5

Transmetallation: 5.5.2.3.1

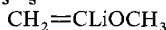


Formation: 5.5.2.2.1, 5.5.2.3.3

Transmetallation: 5.5.2.3.1

**C<sub>3</sub>H<sub>5</sub>LiN<sub>2</sub>O**

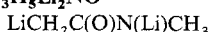
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>5</sub>LiO**

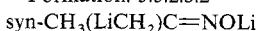
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>5</sub>LiS<sub>3</sub>**

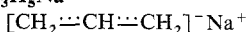
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>5</sub>Li<sub>2</sub>NO**

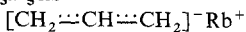
Formation: 5.5.2.3.2



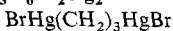
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>5</sub>Na**

Formation: 5.5.3.2.2, 5.5.3.2.3

**C<sub>3</sub>H<sub>5</sub>Rb**

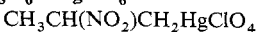
Formation: 5.5.3.2.3

**C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>Hg<sub>2</sub>**

Reaction with RLi: 5.5.2.3.1

**C<sub>3</sub>H<sub>6</sub>Cd**

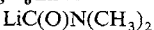
Formation and randomization: 5.7.2.4.3

**C<sub>3</sub>H<sub>6</sub>ClHgNO<sub>6</sub>**

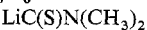
Formation: 5.7.2.3.3

**C<sub>3</sub>H<sub>6</sub>Hg**

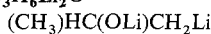
Formation: 5.7.2.4.3

**C<sub>3</sub>H<sub>6</sub>LiNO**

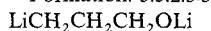
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>6</sub>LiNS**

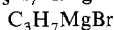
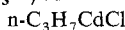
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>6</sub>Li<sub>2</sub>O**

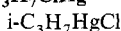
Formation: 5.5.2.3.5



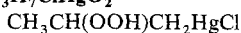
Formation: 5.5.2.3.1

**C<sub>3</sub>H<sub>7</sub>BrMg**Reaction with HgX<sub>2</sub>: 5.7.2.3.1**C<sub>3</sub>H<sub>7</sub>CdCl**

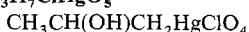
Formation: 5.7.2.3.2

**C<sub>3</sub>H<sub>7</sub>ClHg**

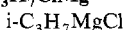
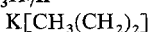
Formation: 5.7.2.3.1

**C<sub>3</sub>H<sub>7</sub>ClHgO<sub>2</sub>**

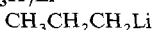
Formation: 5.7.2.3.3

**C<sub>3</sub>H<sub>7</sub>ClHgO<sub>5</sub>**

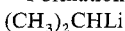
Reaction with nitrite anion: 5.7.2.3.3

**C<sub>3</sub>H<sub>7</sub>ClMg**Reaction with HgX<sub>2</sub>: 5.7.2.3.1**C<sub>3</sub>H<sub>7</sub>K**

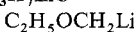
Formation: 5.5.3.2.1

**C<sub>3</sub>H<sub>7</sub>Li**

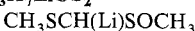
Formation: 5.5.2.2.1, 5.5.2.2.2



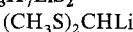
Formation: 5.5.2.2.1

**C<sub>3</sub>H<sub>7</sub>LiO**

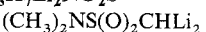
Formation: 5.5.2.3.1

**C<sub>3</sub>H<sub>7</sub>LiOS<sub>2</sub>**

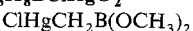
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>7</sub>LiS<sub>2</sub>**

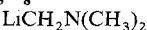
Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>7</sub>Li<sub>2</sub>NO<sub>2</sub>S**

Formation: 5.5.2.3.2

**C<sub>3</sub>H<sub>8</sub>BClHgO<sub>2</sub>**

Formation: 5.7.2.3.7

**C<sub>3</sub>H<sub>8</sub>LiN**

Formation: 5.5.2.3.1

**C<sub>3</sub>H<sub>8</sub>LiNOS**

Formation: 5.5.2.3.2

- C<sub>3</sub>H<sub>8</sub>LiNO<sub>2</sub>S**  
(CH<sub>3</sub>)<sub>2</sub>NS(O)<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>8</sub>LiO<sub>2</sub>PS**  
(CH<sub>3</sub>O)<sub>2</sub>P(S)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>8</sub>LiO<sub>3</sub>P**  
(CH<sub>3</sub>O)<sub>2</sub>P(O)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>8</sub>LiP**  
(CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>3</sub>H<sub>9</sub>Al**  
(CH<sub>3</sub>)<sub>3</sub>Al  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>3</sub>H<sub>9</sub>BrGe**  
(CH<sub>3</sub>)<sub>3</sub>GeBr  
Formation: 5.7.4, 5.7.4.7  
Reaction with Li metal: 5.5.5.3
- C<sub>3</sub>H<sub>9</sub>BrPb**  
(CH<sub>3</sub>)<sub>3</sub>PbBr  
Reaction with Li metal: 5.5.7.4
- C<sub>3</sub>H<sub>9</sub>BrSi**  
(CH<sub>3</sub>)<sub>3</sub>SiBr  
Formation: 5.7.3
- C<sub>3</sub>H<sub>9</sub>BrSn**  
(CH<sub>3</sub>)<sub>3</sub>SnBr  
Reaction with RAg: 5.6.4.1  
Reaction with Na metal: 5.5.6.3.2
- C<sub>3</sub>H<sub>9</sub>ClGe**  
(CH<sub>3</sub>)<sub>3</sub>GeCl  
Reaction with Na-Hg: 5.7.4.3  
Reaction with Li metal: 5.5.5.3
- C<sub>3</sub>H<sub>9</sub>ClPb**  
(CH<sub>3</sub>)<sub>3</sub>PbCl  
Formation: 5.7.6.2  
Reaction with Zn metal: 5.7.6.2
- C<sub>3</sub>H<sub>9</sub>ClSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCl  
Formation: 5.7.3.3, 5.7.3.5, 5.7.4.7  
Reaction with Na-Hg: 5.7.3.2
- C<sub>3</sub>H<sub>9</sub>ClSn**  
(CH<sub>3</sub>)<sub>3</sub>SnCl  
Formation: 5.7.5.4  
Reaction with Li metal: 5.5.6.3.1  
Reaction with K<sup>+</sup>[C<sub>10</sub>H<sub>8</sub>]<sup>-</sup>: 5.5.6.3.3  
Reaction with Na metal: 5.5.6.3.2
- C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>GeHgSi**  
(CH<sub>3</sub>)<sub>3</sub>SiHgGeCl<sub>3</sub>  
Formation: 5.7.4.7
- C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>HgSi<sub>2</sub>**  
(CH<sub>3</sub>)<sub>3</sub>SiHgSiCl<sub>3</sub>  
Formation: 5.7.3.3
- C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>Si<sub>2</sub>**  
(CH<sub>3</sub>)<sub>3</sub>SiSiCl<sub>3</sub>  
Formation: 5.7.3.3
- C<sub>3</sub>H<sub>9</sub>Cl<sub>3</sub>Si<sub>2</sub>**  
(CH<sub>3</sub>)<sub>3</sub>SiSiCl<sub>3</sub>  
Formation: 5.7.3.3
- C<sub>3</sub>H<sub>9</sub>CrN<sub>3</sub>O<sub>3</sub>**  
(CO)<sub>3</sub>Cr(NH<sub>3</sub>)<sub>3</sub>  
Reaction with PhB(OH)<sub>2</sub>: 5.7.2.3.7
- C<sub>3</sub>H<sub>9</sub>GeLi**  
(CH<sub>3</sub>)<sub>3</sub>GeLi  
Formation: 5.5.5.3, 5.5.5.6
- C<sub>3</sub>H<sub>9</sub>Hg<sub>3</sub>O<sub>4</sub>P**  
(CH<sub>3</sub>HgO)<sub>3</sub>PO  
Formation: 5.7.2.3.2
- C<sub>3</sub>H<sub>9</sub>KPb**  
K[(CH<sub>3</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.3
- C<sub>3</sub>H<sub>9</sub>KSi**  
K[(CH<sub>3</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.2.1, 5.5.4.2.2
- C<sub>3</sub>H<sub>9</sub>KSn**  
K[(CH<sub>3</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6.2.3, 5.5.6.3.3
- C<sub>3</sub>H<sub>9</sub>LiPb**  
(CH<sub>3</sub>)<sub>3</sub>PbLi  
Formation: 5.5.7.3, 5.5.7.4
- C<sub>3</sub>H<sub>9</sub>LiSi**  
(CH<sub>3</sub>)<sub>3</sub>SiLi  
Formation: 5.5.3.3.3, 5.5.4.2.1, 5.5.4.2.2, 5.5.4.6, 5.5.5.6
- C<sub>3</sub>H<sub>9</sub>LiSn**  
(CH<sub>3</sub>)<sub>3</sub>SnLi  
Formation: 5.5.6.2.1, 5.5.6.3.1, 5.5.6.5, 5.5.6.6
- C<sub>3</sub>H<sub>9</sub>NaOSi**  
Na[(CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>O)Si]  
Formation: 5.5.4.2.2
- C<sub>3</sub>H<sub>9</sub>NaO<sub>2</sub>Si**  
Na[CH<sub>3</sub>(CH<sub>3</sub>O)<sub>2</sub>Si]  
Formation: 5.5.4.2.2
- C<sub>3</sub>H<sub>9</sub>NaPb**  
Na[(CH<sub>3</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.4
- C<sub>3</sub>H<sub>9</sub>NaSi**  
Na[(CH<sub>3</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.2.2
- C<sub>3</sub>H<sub>9</sub>NaSn**  
Na[(CH<sub>3</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6.3.2, 5.5.6.4, 5.5.6.5
- C<sub>3</sub>H<sub>10</sub>Sn**  
(CH<sub>3</sub>)<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3  
Reaction with Na metal: 5.5.6.4
- C<sub>3</sub>H<sub>12</sub>Ge<sub>2</sub>Hg**  
H<sub>3</sub>GeHgGe(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.7.4, 5.7.4.7

- Reaction with  $\text{H}_3\text{GeX}$ : 5.7.4  
 **$\text{C}_3\text{H}_{12}\text{HgSi}_2$**   
 $\text{H}_3\text{SiHgSi}(\text{CH}_3)_3$   
 Formation: 5.7.3  
 Reaction with  $\text{H}_3\text{SiX}$ : 5.7.3  
 **$\text{C}_3\text{Li}_2\text{O}_2$**   
 $\text{LiC}\equiv\text{CCO}_2\text{Li}$   
 Formation: 5.5.2.3.2  
 **$\text{C}_3\text{Li}_4$**   
 $\text{Li}_3\text{CC}\equiv\text{CLi}$   
 Formation: 5.5.2.3.2  
 **$\text{C}_3\text{Li}_8$**   
 $\text{Li}_3\text{CC}(\text{Li})_2\text{CLi}_3$   
 Formation: 5.5.2.2.1  
 **$\text{C}_4\text{ClF}_9\text{Hg}$**   
 $(\text{CF}_3)_3\text{CHgCl}$   
 Formation: 5.7.2.3.3  
 **$\text{C}_4\text{Cl}_3\text{LiS}$**   
 $\text{ClCCCClCClSCLi}$   
 Formation: 5.5.2.3.3  
 **$\text{C}_4\text{Cl}_4\text{F}_6\text{Zn}$**   
 $(\text{CF}_3\text{CCl}_2)_2\text{Zn}$   
 Formation: 5.7.2.2.1  
 **$\text{C}_4\text{Cl}_6\text{Hg}$**   
 $(\text{Cl}_2\text{C}=\text{CCl})_2\text{Hg}$   
 Formation: 5.7.2.3.4  
 **$\text{C}_4\text{CuF}_9$**   
 $\text{CuC}(\text{CF}_3)_3$   
 Formation: 5.6.4.2  
 **$\text{C}_4\text{F}_6\text{Hg}$**   
 $(\text{CF}_2=\text{CF})_2\text{Hg}$   
 Formation: 5.7.2.3.1  
 **$\text{C}_4\text{F}_6\text{HgN}_4$**   
 $\text{Hg}[\text{C}(\text{N}_2)\text{CF}_3]_2$   
 Formation: 5.7.2.3.4  
 **$\text{C}_4\text{F}_6\text{HgO}_4$**   
 $\text{Hg}[\text{OC}(\text{O})\text{CF}_3]_2$   
 Reaction with alkenes: 5.7.2.3.4  
 Reaction with arenes: 5.7.2.3.4  
 Reaction with ketenes: 5.7.2.3.3  
 **$\text{C}_4\text{F}_{10}\text{Hg}$**   
 $(\text{C}_2\text{F}_5)_2\text{Hg}$   
 Formation: 5.7.2.3.7  
 **$\text{C}_4\text{H}_2\text{AuK}$**   
 $\text{K}[\text{Au}(\text{C}\equiv\text{CH})_2]$   
 Formation: 5.6.4.3  
 **$\text{C}_4\text{H}_2\text{BrLiO}$**   
 $\text{CHCHCBrC}(\text{Li})\text{O}$   
 Formation: 5.5.2.3.2  
 **$\text{C}_4\text{H}_2\text{BrLiS}$**   
 $\text{BrCCHCHSCLi}$   
 Formation: 5.5.2.3.3  
 $\text{HCCHCBrSCLi}$   
 Formation: 5.5.2.3.3  
 $\text{HCC}(\text{Li})\text{CHSCBr}$   
 Formation: 5.5.2.3.3  
 **$\text{C}_4\text{H}_2\text{CILiS}$**   
 $\text{LiCCHCHSCLi}$   
 Formation: 5.5.2.3.3  
 **$\text{C}_4\text{H}_2\text{Cl}_2\text{F}_6\text{Hg}$**   
 $\text{Hg}(\text{CHClCF}_3)_2$   
 Formation: 5.7.2.3.5  
 **$\text{C}_4\text{H}_2\text{Cl}_2\text{Hg}_2\text{O}$**   
 $\text{ClHgCCHCHC}(\text{HgCl})\text{O}$   
 Formation: 5.7.2.3.4  
 **$\text{C}_4\text{H}_2\text{Cl}_2\text{Hg}_2\text{S}$**   
 $\text{ClHgCCHCHC}(\text{HgCl})\text{S}$   
 Formation: 5.7.2.3.4  
 **$\text{C}_4\text{H}_2\text{FLiS}$**   
 $\text{HCC}(\text{Li})\text{CHSCF}$   
 Formation: 5.5.2.3.3  
 **$\text{C}_4\text{H}_2\text{ILiS}$**   
 $\text{CHCHClC}(\text{Li})\text{S}$   
 Formation: 5.5.2.3.2  
 $\text{LiCCHClCHS}$   
 Formation: 5.5.2.3.2  
 **$\text{C}_4\text{H}_2\text{Li}_2\text{O}_2$**   
 $\text{LiCH}_2\text{C}\equiv\text{CCO}_2\text{Li}$   
 Formation: 5.5.2.3.2  
 **$\text{C}_4\text{H}_2\text{Li}_2\text{S}$**   
 $\text{LiCCHCHC}(\text{Li})\text{S}$   
 Formation: 5.5.2.3.2  
 **$\text{C}_4\text{H}_2\text{NaS}$**   
 $[(\text{SC}(\text{Cl})\text{CHCHC})]^- \text{Na}^+$   
 Formation: 5.5.3.2.5  
 **$\text{C}_4\text{H}_3\text{BrCd}$**   
 $\text{H}_2\text{C}=\text{CHC}\equiv\text{CCdBr}$   
 Formation: 5.7.2.3.1  
 **$\text{C}_4\text{H}_3\text{BrMg}$**   
 $\text{H}_2\text{C}=\text{CHC}\equiv\text{CMgBr}$   
 Reaction with  $\text{CdX}_2$ : 5.7.2.3.1  
 **$\text{C}_4\text{H}_3\text{ClHgO}$**   
 $\text{CHCHCHCHOCHgCl}$   
 Formation: 5.7.2.3.7, 5.7.2.3.4  
 **$\text{C}_4\text{H}_3\text{ClHgS}$**   
 $\text{CHCHCHSCHgCl}$   
 Formation: 5.7.2.3.7, 5.7.2.3.4  
 **$\text{C}_4\text{H}_3\text{ClS}$**   
 $\text{SCCICHCHCH}$   
 Reaction with Na-Hg: 5.5.3.2.5



**C<sub>4</sub>H<sub>3</sub>LiO**

Formation: 5.5.2.3.3

**C<sub>4</sub>H<sub>3</sub>LiS**

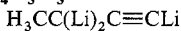
Formation: 5.5.2.3.3, 5.5.2.3.5

**C<sub>4</sub>H<sub>3</sub>LiS<sub>2</sub>**

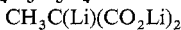
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>3</sub>LiSe**

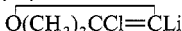
Formation: 5.5.2.3.3

**C<sub>4</sub>H<sub>3</sub>Li<sub>3</sub>**

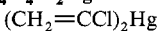
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>3</sub>Li<sub>3</sub>O<sub>4</sub>**

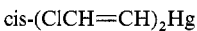
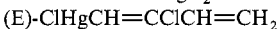
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>4</sub>ClLiO**

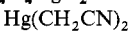
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>4</sub>Cl<sub>2</sub>Hg**

Formation: 5.7.2.3.1

Reaction with HgX<sub>2</sub>: 5.7.2.3.2

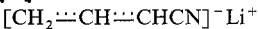
Formation: 5.7.2.3.3

**C<sub>4</sub>H<sub>4</sub>HgN<sub>2</sub>**

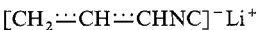
Formation: 5.7.2.3.1

**C<sub>4</sub>H<sub>4</sub>HgN<sub>6</sub>O<sub>12</sub>**

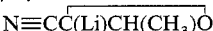
Formation: 5.7.2.3.3

**C<sub>4</sub>H<sub>4</sub>LiN**

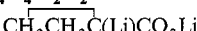
Formation: 5.5.2.3.2



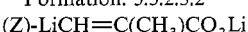
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>4</sub>LiNO**

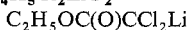
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>4</sub>Li<sub>2</sub>O<sub>2</sub>**

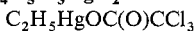
Formation: 5.5.2.3.2



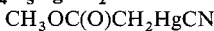
Formation: 5.5.2.3.3

**C<sub>4</sub>H<sub>5</sub>BO<sub>2</sub>S**Reaction with HgX<sub>2</sub>: 5.7.2.3.7**C<sub>4</sub>H<sub>5</sub>BO<sub>3</sub>**Reaction with HgX<sub>2</sub>: 5.7.2.3.7**C<sub>4</sub>H<sub>5</sub>Cl<sub>2</sub>LiO<sub>2</sub>**

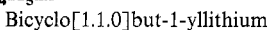
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub>HgO<sub>2</sub>**

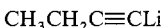
Formation: 5.7.2.3.2

**C<sub>4</sub>H<sub>5</sub>HgNO<sub>2</sub>**

Formation: 5.7.2.3.2

**C<sub>4</sub>H<sub>5</sub>Li**

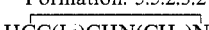
Formation: 5.5.2.3.2



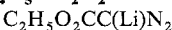
Formation: 5.5.2.2.4

**C<sub>4</sub>H<sub>5</sub>LiN<sub>2</sub>**

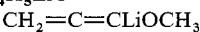
Formation: 5.5.2.3.2



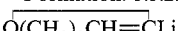
Formation: 5.5.2.3.3

**C<sub>4</sub>H<sub>5</sub>LiN<sub>2</sub>O<sub>2</sub>**

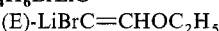
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>5</sub>LiO**

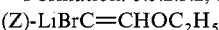
Formation: 5.5.2.3.2



Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>6</sub>BrLiO**

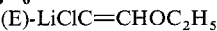
Formation: 5.5.2.3.2, 5.5.2.3.3



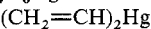
Formation: 5.5.2.3.5

**C<sub>4</sub>H<sub>6</sub>ClLi**

Formation: 5.5.2.3.1

**C<sub>4</sub>H<sub>6</sub>ClLiO**

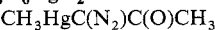
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>6</sub>Hg**

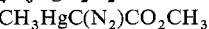
Formation: 5.7.2.3.1

Reaction with R<sub>2</sub>Cd: 5.7.2.4.3

Reaction with Li metal: 5.5.2.2.2

**C<sub>4</sub>H<sub>6</sub>HgN<sub>2</sub>O**

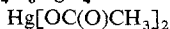
Formation: 5.7.2.3.4

**C<sub>4</sub>H<sub>6</sub>HgN<sub>2</sub>O<sub>2</sub>**

Formation: 5.7.2.3.4

**C<sub>4</sub>H<sub>6</sub>HgO<sub>2</sub>**

Formation: 5.7.2.3.7

**C<sub>4</sub>H<sub>6</sub>HgO<sub>4</sub>**

Decarboxylation: 5.7.2.3.7

Reaction with RSO<sub>2</sub>M: 5.7.2.3.7Reaction with (C<sub>6</sub>H<sub>5</sub>)<sub>6</sub>Pb<sub>2</sub>: 5.7.6.2Reaction with RB(OR')<sub>2</sub>: 5.7.2.3.7

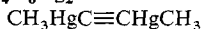
Reaction with aliphatics: 5.7.2.3.4

Reaction with alkenes: 5.7.2.3.3

Reaction with arenes: 5.7.2.3.4

Reaction with arylhydrazines: 5.7.2.3.6

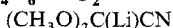
Reaction with alkenes: 5.7.2.3.3

**C<sub>4</sub>H<sub>6</sub>Hg<sub>2</sub>**

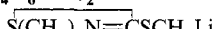
Formation: 5.7.2.3.4

**C<sub>4</sub>H<sub>6</sub>LiN**

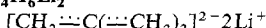
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>6</sub>LiNO<sub>2</sub>**

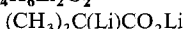
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>6</sub>LiNS<sub>2</sub>**

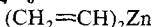
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>6</sub>Li<sub>2</sub>**

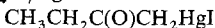
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>6</sub>Li<sub>2</sub>O<sub>2</sub>**

Formation: 5.5.2.3.5

**C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>**Reaction with Hg(OAc)<sub>2</sub>: 5.7.2.3.3**C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>S**Reaction with Hg(OAc)<sub>2</sub>: 5.7.2.3.3**C<sub>4</sub>H<sub>6</sub>Zn**

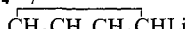
Formation: 5.7.2.3.1

**C<sub>4</sub>H<sub>7</sub>BrMg**Reaction with CdX<sub>2</sub>: 5.7.2.3.1**C<sub>4</sub>H<sub>7</sub>ClMg**Reaction with HgX<sub>2</sub>: 5.7.2.3.1**C<sub>4</sub>H<sub>7</sub>ClZn**Reaction with ArCH=CH<sub>2</sub>: 5.7.2.4.2**C<sub>4</sub>H<sub>7</sub>HgIO**

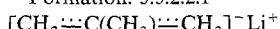
Formation: 5.7.2.3.4



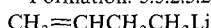
Formation: 5.7.2.3.4

**C<sub>4</sub>H<sub>7</sub>Li**

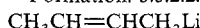
Formation: 5.5.2.2.1



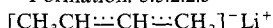
Formation: 5.5.2.3.2



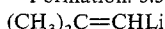
Formation: 5.5.2.2.2



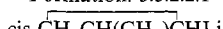
Formation: 5.5.2.2.5



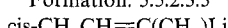
Formation: 5.5.2.3.1, 5.5.2.3.2



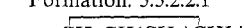
Formation: 5.5.2.2.1



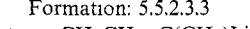
Formation: 5.5.2.3.3



Formation: 5.5.2.2.1



Formation: 5.5.2.3.3



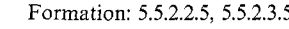
Formation: 5.5.2.2.1

**C<sub>4</sub>H<sub>7</sub>LiN<sub>2</sub>O**

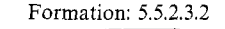
Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>7</sub>LiO**

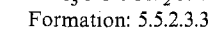
Formation: 5.5.2.2.5, 5.5.2.3.5



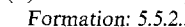
Formation: 5.5.2.3.2



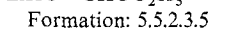
Formation: 5.5.2.3.3



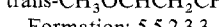
Formation: 5.5.2.3.3



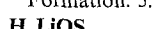
Formation: 5.5.2.3.5



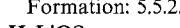
Formation: 5.5.2.3.3



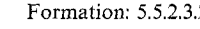
Formation: 5.5.2.3.1, 5.5.2.3.3.

**C<sub>4</sub>H<sub>7</sub>LiOS**

Formation: 5.5.2.3.1

**C<sub>4</sub>H<sub>7</sub>LiOS<sub>2</sub>**

Formation: 5.5.2.3.2

**C<sub>4</sub>H<sub>7</sub>LiO<sub>2</sub>**

Formation: 5.5.2.3.2

- C<sub>4</sub>H<sub>7</sub>LiO<sub>2</sub>** *contd.*  
 $\text{CH}_3\text{OCLi}=\text{CHOCH}_3$   
 Formation: 5.5.2.3.3  
 $\text{LiCH}_2\text{CO}_2\text{C}_2\text{H}_5$   
 Formation: 5.5.2.3.3
- C<sub>4</sub>H<sub>7</sub>LiO<sub>3</sub>S**  
 $\text{S}(\text{O})_2\text{O}(\text{CH}_2)_3\text{CHLi}$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>7</sub>LiS**  
 $\text{CH}_2=\text{C}(\text{Li})\text{SC}_2\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>7</sub>LiS<sub>2</sub>**  
 $\text{S}(\text{CH}_2)_3\text{SCHLi}$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>7</sub>LiS<sub>4</sub>**  
 $\text{S}(\text{CH}_2\text{S})_3\text{CHLi}$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>Tl**  
 $\text{Tl}[\text{MeC}(\text{O})\text{CHC}(\text{O})\text{Me}]$   
 Reaction with LAuCl: 5.6.4.1
- C<sub>4</sub>H<sub>8</sub>Br<sub>2</sub>Zn<sub>2</sub>**  
 $\text{BrZnCH}_2(\text{CH}_2)_2\text{CH}_2\text{ZnBr}$   
 Formation: 5.7.2.2.1
- C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub>Hg**  
 $\text{CH}_3\text{CHClHgCH}(\text{CH}_3)\text{Cl}$   
 Formation: 5.7.2.3.3
- C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub>Hg<sub>2</sub>O**  
 $(\text{ClHgCH}_2\text{CH}_2)_2\text{O}$   
 Formation: 5.7.2.3.3
- C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub>Hg<sub>2</sub>O<sub>2</sub>**  
 $(\text{ClHgCH}_2\text{CH}_2\text{O})_2$   
 Formation: 5.7.2.3.3
- C<sub>4</sub>H<sub>8</sub>LiNO**  
 $\text{LiCH}_2\text{CON}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>8</sub>LiNS<sub>2</sub>**  
 $\text{SCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{SCHLi}$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>8</sub>Li<sub>2</sub>**  
 $\text{LiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>**  
 $\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}$   
 Reaction with Na-K or Cs metal:  
 5.5.3.2.2
- C<sub>4</sub>H<sub>9</sub>BrCd**  
 $\text{C}_4\text{H}_9\text{CdBr}$   
 Formation: 5.7.2.3.1
- C<sub>4</sub>H<sub>9</sub>BrClLiSn**  
 $(\text{CH}_3)_3\text{SnCClBrLi}$   
 Formation: 5.5.2.3.1
- C<sub>4</sub>H<sub>9</sub>BrHg**  
 $\text{C}_3\text{H}_7\text{HgCH}_2\text{Br}$   
 Formation: 5.7.2.3.3
- $\text{HC}(\text{CH}_3)\text{C}_2\text{H}_5\text{HgBr}$   
 Formation: 5.7.2.3.2  
 Reaction with RMgX: 5.7.2.3.2
- s-C<sub>4</sub>H<sub>9</sub>HgBr**  
 Formation: 5.7.2.3.1
- C<sub>4</sub>H<sub>9</sub>BrMg**  
 $\text{C}_4\text{H}_9\text{MgBr}$   
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
 $\text{HC}(\text{CH}_3)\text{C}_2\text{H}_5\text{MgBr}$   
 Reaction with RHgX: 5.7.2.3.2  
**s-C<sub>4</sub>H<sub>9</sub>MgBr**  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>4</sub>H<sub>9</sub>Br<sub>2</sub>LiSi**  
 $(\text{CH}_3)_3\text{SiCBr}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>9</sub>Br<sub>2</sub>LiSn**  
 $(\text{CH}_3)_3\text{SnCBr}_2\text{Li}$   
 Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>4</sub>H<sub>9</sub>CdCl**  
**n-C<sub>4</sub>H<sub>9</sub>CdCl**  
 Formation: 5.7.2.2.1
- C<sub>4</sub>H<sub>9</sub>ClHg**  
 $(\text{CH}_3)_3\text{CHgCl}$   
 Reaction with KI: 5.7.2.3.1  
 $\text{C}_4\text{H}_9\text{HgCl}$   
 Formation: 5.7.2.3.1
- C<sub>4</sub>H<sub>9</sub>ClMg**  
 $\text{C}_4\text{H}_9\text{MgCl}$   
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>4</sub>H<sub>9</sub>Cl<sub>2</sub>LiSi**  
 $(\text{CH}_3)_3\text{SiCCl}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>9</sub>Cl<sub>2</sub>LiSn**  
 $(\text{CH}_3)_3\text{SnCCl}_2\text{Li}$   
 Formation: 5.5.2.3.1
- C<sub>4</sub>H<sub>9</sub>Cs**  
 $\text{Cs}[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2]$   
 Formation: 5.5.3.3.2, 5.5.3.2.3
- C<sub>4</sub>H<sub>9</sub>CsO**  
 $\text{Cs}[(\text{CH}_3)_3\text{CO}]$   
 Reagent for metal-metal exchange:  
 5.5.3.3.2
- C<sub>4</sub>H<sub>9</sub>HgI**  
 $(\text{CH}_3)_3\text{CHgI}$   
 Formation: 5.7.2.3.1  
**n-C<sub>4</sub>H<sub>9</sub>HgI**  
 Formation: 5.7.2.2.1  
**s-C<sub>4</sub>H<sub>9</sub>HgI**  
 Formation: 5.7.2.2.1
- C<sub>4</sub>H<sub>9</sub>K**  
 $\text{K}[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]$   
 Base for metallation reaction: 5.5.3.3.1  
 Formation: 5.5.3.2.1, 5.5.3.2.3, 5.5.3.3.2

- Reaction with alkanes: 5.5.3.2.3  
 Reagent for metal-metal exchange:  
 5.5.3.3.2
- C<sub>4</sub>H<sub>9</sub>KO**  
 K[(CH<sub>3</sub>)<sub>3</sub>CO]  
 Metal exchange with RLi: 5.5.3.3.1  
 Reagent for metal-metal exchange:  
 5.5.3.3.2
- C<sub>4</sub>H<sub>9</sub>Li**  
 CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)Li  
 Formation: 5.5.2.2.1, 5.5.2.3.1, 5.5.2.2.5  
 (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>Li  
 Formation: 5.5.2.2.1  
 (CH<sub>3</sub>)<sub>3</sub>CLi  
 Addition to acetylenes: 5.5.2.3.4  
 Addition to olefins: 5.5.2.3.4  
 Formation: 5.5.2.2.1, 5.5.2.2.5  
 Reaction with aromatic protons:  
 5.5.2.3.2  
 CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
 Addition to acetylenes: 5.5.2.3.4  
 Addition to olefins: 5.5.2.3.4  
 Formation: 5.5.2.2.1, 5.5.2.3.5  
 Reaction with RC≡CH: 5.5.2.3.2  
 Reaction with RX: 5.5.2.3.3  
 Reaction with allenes: 5.5.2.3.2  
 Reaction with allylic hydrogens: 5.5.2.3.2  
 Reaction with benzylic hydrogens:  
 5.5.2.3.2  
 Reaction with propargylic hydrogens:  
 5.5.2.3.2  
 Substrate in metal-metal exchange:  
 5.5.3.3.2  
 Transmetallation: 5.5.2.3.1, 5.5.3.3.1
- C<sub>4</sub>H<sub>9</sub>LiN<sub>2</sub>Si**  
 (CH<sub>3</sub>)<sub>3</sub>SiC(Li)N<sub>2</sub>  
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>9</sub>LiO**  
 (CH<sub>3</sub>)<sub>2</sub>C(OCH<sub>3</sub>)Li  
 Formation: 5.5.2.2.5, 5.5.2.3.5  
 i-C<sub>3</sub>H<sub>7</sub>OCH<sub>2</sub>Li  
 Formation: 5.5.2.3.1
- C<sub>4</sub>H<sub>9</sub>LiOS<sub>2</sub>**  
 CH<sub>3</sub>SC(Li)CH<sub>3</sub>SOCH<sub>3</sub>  
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>9</sub>Li<sub>2</sub>NO**  
 LiCH<sub>2</sub>N(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OLi  
 Formation: 5.5.2.3.1
- C<sub>4</sub>H<sub>9</sub>Na**  
 Na[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>]  
 Formation: 5.5.3.3.2  
 Reagent for metal-metal exchange:  
 5.5.3.3.2
- C<sub>4</sub>H<sub>9</sub>NaO**  
 Na[OC(CH<sub>3</sub>)<sub>3</sub>]  
 Base for metallation reaction: 5.5.3.3.1  
 Reagent for metal-metal exchange:  
 5.5.3.3.2
- C<sub>4</sub>H<sub>10</sub>AlCl**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlCl  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>4</sub>H<sub>10</sub>Br<sub>2</sub>SiZn<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>3</sub>SiCH(ZnBr)<sub>2</sub>  
 Formation: 5.7.2.2.1
- C<sub>4</sub>H<sub>10</sub>Cd**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cd  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.2  
 Reaction with R<sub>3</sub>GeH: 5.7.4.2  
 Reaction with R<sub>3</sub>SiH: 5.7.3.3  
 Reaction with R<sub>3</sub>SnH: 5.7.5.2.2
- C<sub>4</sub>H<sub>10</sub>ClLiSi**  
 (CH<sub>3</sub>)<sub>3</sub>SiCHClLi  
 Formation: 5.5.2.3.2
- C<sub>4</sub>H<sub>10</sub>Cl<sub>2</sub>Sn**  
 (CH<sub>3</sub>)<sub>3</sub>SnCCl<sub>2</sub>H  
 Transmetallation: 5.5.2.3.1
- C<sub>4</sub>H<sub>10</sub>Hg**  
 (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Hg  
 Formation: 5.5.2.3.1  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.2  
 Reaction with Ph<sub>2</sub>GeH<sub>2</sub>: 5.7.4.2  
 Reaction with Li metal: 5.5.2.2.2  
 Reaction with Na metal: 5.5.3.2.3  
 Reaction with Ph<sub>3</sub>SnH: 5.7.5.2.3  
 Reaction with R<sub>2</sub>GeXH: 5.7.4.2  
 Reaction with R<sub>3</sub>GeH: 5.7.4.2  
 Reaction with R<sub>3</sub>SiH: 5.7.3.3  
 Reaction with R<sub>3</sub>SnH: 5.7.5.2.3  
 Reaction with R<sub>3</sub>SiSiR<sub>2</sub>H: 5.7.3.3  
 Reaction with Zn metal: 5.7.2.2.2
- C<sub>4</sub>H<sub>10</sub>Na<sub>2</sub>Sn**  
 Na<sub>2</sub>[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Sn]  
 Formation: 5.5.6.2.2
- C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>S**  
 (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>SO<sub>2</sub>  
 Reaction with Zn metal: 5.7.2.2.1
- C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>SZn**  
 C<sub>2</sub>H<sub>5</sub>ZnOSO<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>  
 Formation: 5.7.2.2.1
- C<sub>4</sub>H<sub>10</sub>Zn**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn  
 Formation: 5.7.2.2.1, 5.7.2.2.2  
 Reaction with R<sub>3</sub>B: 5.7.2.4.3  
 Reaction with R<sub>3</sub>SnH: 5.7.5.2.1

**C<sub>4</sub>H<sub>10</sub>Zn** *contd.*

- Reaction with Ph<sub>3</sub>SnH: 5.7.5.2.1  
 Reaction with R<sub>3</sub>GeH: 5.7.4.2  
 Reaction with R<sub>3</sub>SiH: 5.7.3.3  
 Reaction with R<sub>3</sub>SnH: 5.7.5.2.1  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.2  
 Reaction with fluorene and carboranes:  
 5.7.2.4.1

**C<sub>4</sub>H<sub>11</sub>ClHgSi**

- (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>HgCl  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1

**C<sub>4</sub>H<sub>11</sub>ClMgSi**

- (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>MgCl  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.1

**C<sub>4</sub>H<sub>11</sub>ClSi**

- (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Cl  
 Reaction with Li metal: 5.5.2.2.1

**C<sub>4</sub>H<sub>11</sub>Cl<sub>3</sub>GeHgSi**

- (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>HgGeCl<sub>3</sub>  
 Formation: 5.7.4.2

**C<sub>4</sub>H<sub>11</sub>CsSi**

- Cs[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]  
 Base for metallation reaction: 5.5.3.3.1

**C<sub>4</sub>H<sub>11</sub>KS**

- K[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]  
 Base for metallation reaction: 5.5.3.3.1

**C<sub>4</sub>H<sub>11</sub>LiOSi**

- LiCH<sub>2</sub>OSi(CH<sub>3</sub>)<sub>3</sub>  
 Formation: 5.5.2.3.1

**C<sub>4</sub>H<sub>11</sub>LiSi**

- (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Li  
 Formation: 5.5.2.2.1, 5.5.2.2.5, 5.5.2.3.1,  
 5.5.2.3.3  
 Reaction with CuI: 5.6.4

**C<sub>4</sub>H<sub>11</sub>NaSi**

- Na[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]  
 Base for metallation reaction: 5.5.3.3.1

**C<sub>4</sub>H<sub>11</sub>P**

- (CH<sub>3</sub>)<sub>3</sub>P=CH<sub>2</sub>  
 Reaction with CuX, AgX, AuX and  
 RAu-Ylid complexes: 5.6.4.3

**C<sub>4</sub>H<sub>11</sub>RbSi**

- Rb[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]  
 Base for metallation reaction: 5.5.3.3.1

**C<sub>4</sub>H<sub>12</sub>Cl<sub>2</sub>HgSi<sub>2</sub>**

- [(CH<sub>3</sub>)<sub>2</sub>ClSi]<sub>2</sub>Hg  
 Formation: 5.7.3.3  
 (CH<sub>3</sub>)<sub>3</sub>SiHgSiCl<sub>2</sub>CH<sub>3</sub>  
 Formation: 5.7.3.5

**C<sub>4</sub>H<sub>12</sub>Cl<sub>2</sub>Si<sub>2</sub>**

- (CH<sub>3</sub>)<sub>3</sub>SiSiCl<sub>2</sub>CH<sub>3</sub>  
<sup>1</sup>H-NMR: 5.7.3

**C<sub>4</sub>H<sub>12</sub>GeO**

- (CH<sub>3</sub>)<sub>3</sub>GeOCH<sub>3</sub>  
 Reaction with (R<sub>3</sub>Si)<sub>2</sub>Hg: 5.7.3.5

**C<sub>4</sub>H<sub>12</sub>Li<sub>2</sub>Zn**

- Li<sub>2</sub>[Zn(CH<sub>3</sub>)<sub>4</sub>]  
 Formation and structure: 5.7.2.4.3

**C<sub>4</sub>H<sub>12</sub>OSi**

- (CH<sub>3</sub>)<sub>3</sub>SiOCH<sub>3</sub>  
 Formation: 5.7.3.5

**C<sub>4</sub>H<sub>12</sub>OSn**

- (CH<sub>3</sub>)<sub>3</sub>SnOCH<sub>3</sub>  
 Reaction with (R<sub>3</sub>Si)<sub>2</sub>Hg: 5.7.3.5

**C<sub>4</sub>H<sub>12</sub>Pb**

- (CH<sub>3</sub>)<sub>4</sub>Pb  
 Reaction with group-IA: 5.5.7.3

**C<sub>4</sub>H<sub>12</sub>Si**

- (CH<sub>3</sub>)<sub>4</sub>Si  
 Formation: 5.7.4.2

**C<sub>4</sub>H<sub>12</sub>Sn**

- (CH<sub>3</sub>)<sub>4</sub>Sn  
 Formation: 5.5.6  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
 Reaction with Na metal: 5.5.6.5  
 (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SnH<sub>2</sub>  
 Reaction with R<sub>2</sub>Hg: 5.7.5.2.3

**C<sub>4</sub>H<sub>14</sub>HgSi<sub>2</sub>**

- [(CH<sub>3</sub>)<sub>2</sub>HSi]<sub>2</sub>Hg  
 Formation: 5.7.3.2

**C<sub>4</sub>H<sub>22</sub>B<sub>20</sub>Hg**

- Hg(C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>  
 Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.6

**C<sub>5</sub>AgF<sub>10</sub>**

- Ag[CF<sub>3</sub>CF=CF(CF<sub>3</sub>)<sub>2</sub>]  
 Formation: 5.6.4.2

**C<sub>5</sub>Cl<sub>4</sub>LiN**

- 2-LiC<sub>5</sub>Cl<sub>4</sub>N  
 Formation: 5.5.2.3.3  
 3-LiC<sub>5</sub>Cl<sub>4</sub>N  
 Formation: 5.5.2.3.3  
 4-LiC<sub>5</sub>Cl<sub>4</sub>N  
 Formation: 5.5.2.3.3

**C<sub>5</sub>F<sub>11</sub>Li**

- (CF<sub>3</sub>)<sub>3</sub>CCF<sub>2</sub>Li  
 Formation: 5.5.2.3.2

**C<sub>5</sub>F<sub>12</sub>Hg**

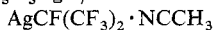
- (CF<sub>3</sub>)<sub>3</sub>CHGCF<sub>3</sub>  
 Formation: 5.7.2.3.3

**C<sub>5</sub>H<sub>2</sub>LiNSe**

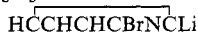
- LiCCHCHC(CN)Se  
 Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>2</sub>Li<sub>2</sub>O<sub>3</sub>**

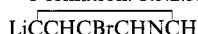
- CHCHC[C(O)OLi]C(Li)O  
 Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>3</sub>AgF<sub>7</sub>N**

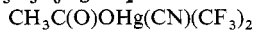
Formation: 5.6.4

**C<sub>5</sub>H<sub>3</sub>BrLiN**

Formation: 5.5.2.3.3



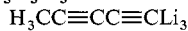
Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>3</sub>F<sub>6</sub>HgNO<sub>2</sub>**

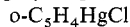
Formation: 5.7.2.3.4

**C<sub>5</sub>H<sub>3</sub>Li<sub>2</sub>N**

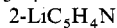
Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>3</sub>Li<sub>3</sub>**

Formation: 5.5.2.3.2

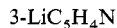
**C<sub>5</sub>H<sub>4</sub>ClHg**

Formation: 5.7.2.3.7

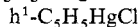
**C<sub>5</sub>H<sub>4</sub>LiN**

Formation: 5.5.2.3.3

Reaction with RAg: 5.6.4.1



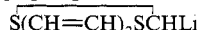
Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>4</sub>ClHg**

Formation: 5.7.2.3.1

**C<sub>5</sub>H<sub>4</sub>Li**

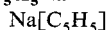
Formation: 5.5.2.2.4, 5.5.2.3.2

**C<sub>5</sub>H<sub>4</sub>LiS<sub>2</sub>**

Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>5</sub>Li<sub>2</sub>N**

Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>5</sub>Na**

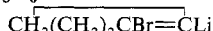
Formation: 5.5.3.3.1

Reaction with HgX<sub>2</sub>: 5.7.2.3.1

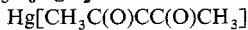
Reaction with AgX: 5.6.4.1

Reaction with ZnX<sub>2</sub>: 5.7.2.3.1**C<sub>5</sub>H<sub>5</sub>Tl**Reaction with HgX<sub>2</sub>: 5.7.2.3.1

Reaction with RCuL, RAu(I)L and R\*

Au(III)X<sub>2</sub>L: 5.6.4.1**C<sub>5</sub>H<sub>6</sub>BrLi**

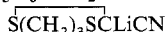
Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>6</sub>HgO<sub>2</sub>**

Formation: 5.7.2.3.4

**C<sub>5</sub>H<sub>6</sub>LiNS**

Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>6</sub>LiNS<sub>2</sub>**

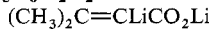
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>6</sub>Li<sub>2</sub>**

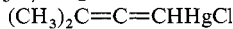
Formation: 5.5.2.3.2



Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>6</sub>Li<sub>2</sub>O<sub>2</sub>**

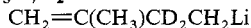
Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>7</sub>ClHg**

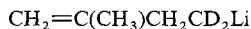
Formation: 5.7.2.3.7

**C<sub>5</sub>H<sub>7</sub>ClHgO<sub>2</sub>**

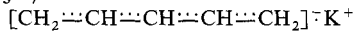
Formation: 5.7.2.3.3

**C<sub>5</sub>H<sub>7</sub>D<sub>2</sub>Li**

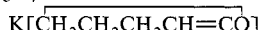
Formation: 5.5.2.3.4



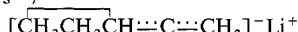
Formation: 5.5.2.3.4

**C<sub>5</sub>H<sub>7</sub>K**

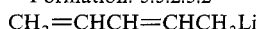
Formation: 5.5.3.2.5, 5.5.3.3.1

Reaction with ZnX<sub>2</sub>: 5.7.2.3.1**C<sub>5</sub>H<sub>7</sub>KO**

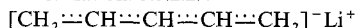
Formation: 5.5.3.3.1

**C<sub>5</sub>H<sub>7</sub>Li**

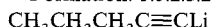
Formation: 5.5.2.3.2



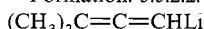
Formation: 5.5.2.2.4



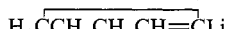
Formation: 5.5.2.3.2



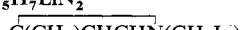
Formation: 5.5.2.2.4



Formation: 5.5.2.3.2



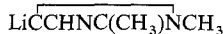
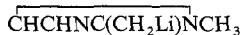
Formation: 5.5.2.2.1

**C<sub>5</sub>H<sub>7</sub>LiN<sub>2</sub>**

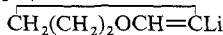
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>7</sub>LiN<sub>2</sub>** *contd.*

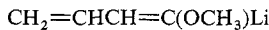
Formation: 5.5.2.3.2



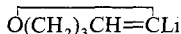
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>7</sub>LiO**

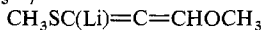
Formation: 5.5.2.3.3



Formation: 5.5.2.3.2



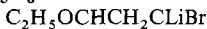
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>7</sub>LiOS**

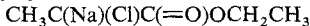
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>7</sub>LiS**

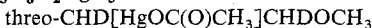
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>8</sub>**Reaction with Hg(OAc)<sub>2</sub>: 5.7.2.3.3**C<sub>5</sub>H<sub>8</sub>BrLiO**

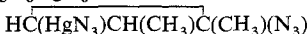
Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>8</sub>ClNaO<sub>2</sub>**

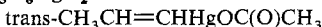
Formation: 5.5.3.3.1

**C<sub>5</sub>H<sub>8</sub>D<sub>2</sub>HgO<sub>3</sub>**

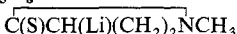
Formation: 5.7.2.3.3

**C<sub>5</sub>H<sub>8</sub>HgN<sub>6</sub>**

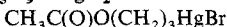
Formation: 5.7.2.3.3

**C<sub>5</sub>H<sub>8</sub>HgO<sub>2</sub>**

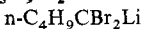
Formation: 5.7.2.3.2

**C<sub>5</sub>H<sub>8</sub>LiNS**

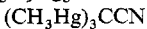
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>9</sub>BrHgO<sub>2</sub>**

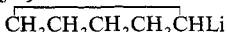
Formation: 5.7.2.3.3

**C<sub>5</sub>H<sub>9</sub>Br<sub>2</sub>Li**

Formation: 5.5.2.3.2, 5.5.2.3.3

**C<sub>5</sub>H<sub>9</sub>Hg<sub>3</sub>N**

Formation: 5.7.2.3.4

**C<sub>5</sub>H<sub>9</sub>Li**

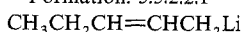
Formation: 5.5.2.2.1



Formation: 5.5.2.2.1



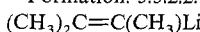
Formation: 5.5.2.2.1



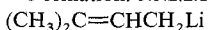
Formation: 5.5.2.2.5



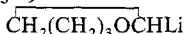
Formation: 5.5.2.2.1



Formation: 5.5.2.2.1



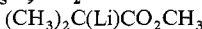
Formation: 5.5.2.2.5

**C<sub>5</sub>H<sub>9</sub>LiO**

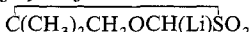
Formation: 5.5.2.2.5, 5.5.2.3.5

**C<sub>5</sub>H<sub>9</sub>LiOS**

Formation: 5.5.2.3.1

**C<sub>5</sub>H<sub>9</sub>LiO<sub>2</sub>**

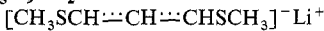
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>9</sub>LiO<sub>3</sub>S**

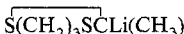
Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>9</sub>LiO<sub>4</sub>**

Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>9</sub>LiS<sub>2</sub>**

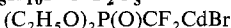
Formation: 5.5.2.3.2



Formation: 5.5.2.3.2

**C<sub>5</sub>H<sub>9</sub>LiS<sub>3</sub>**

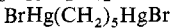
Formation: 5.5.2.3.1

**C<sub>5</sub>H<sub>10</sub>BrCdF<sub>2</sub>O<sub>3</sub>P**

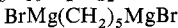
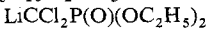
Formation: 5.7.2.2.1

**C<sub>5</sub>H<sub>10</sub>BrLi**

Formation: 5.5.2.3.3

**C<sub>5</sub>H<sub>10</sub>Br<sub>2</sub>Hg<sub>2</sub>**

Formation: 5.7.2.3.1

**C<sub>5</sub>H<sub>10</sub>Br<sub>2</sub>Mg<sub>2</sub>**Reaction with HgX<sub>2</sub>: 5.7.2.3.1**C<sub>5</sub>H<sub>10</sub>Cl<sub>2</sub>LiO<sub>3</sub>P**

Formation: 5.5.2.3.3

- C<sub>5</sub>H<sub>10</sub>LiNO**  
 $\text{CH}_3\text{CH}(\text{Li})\text{C}(\text{O})\text{N}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>10</sub>LiNO<sub>2</sub>S**  
 $\text{LiC}(\text{S})\text{N}(\text{CH}_2\text{OCH}_3)_2$   
 Formation: 5.5.2.3.2  
 $\text{SO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{CHLi}$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>10</sub>LiNO<sub>3</sub>**  
 $\text{LiC}(\text{O})\text{N}(\text{CH}_2\text{OCH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>10</sub>LiNS<sub>3</sub>**  
 $\text{CH}_3\text{SCHLiSC}(\text{S})\text{N}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>10</sub>LiNSi**  
 $(\text{CH}_3)_3\text{SiCH}(\text{CN})\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>10</sub>Li<sub>2</sub>**  
 $\text{LiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>5</sub>H<sub>10</sub>Li<sub>2</sub>O**  
 $(i\text{-C}_3\text{H}_7)\text{HC}(\text{OLi})\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.5
- C<sub>5</sub>H<sub>10</sub>Li<sub>2</sub>O<sub>2</sub>Si**  
 $(\text{CH}_3)_3\text{SiCH}(\text{Li})\text{CO}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>10</sub>OZn**  
 $\text{CH}_3\text{CH}=\text{CHCH}_2\text{ZnOCH}_3$   
 Reaction with  $\text{ArCH}=\text{CH}_2$ : 5.7.2.4.2
- C<sub>5</sub>H<sub>11</sub>BrMg**  
 $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{MgBr}$   
 Reaction with  $\text{CdX}_2$ : 5.7.2.3.1  
 $\text{cyclo-C}_5\text{H}_{11}\text{MgBr}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- C<sub>5</sub>H<sub>11</sub>ClLiO<sub>2</sub>PS**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{CH}(\text{Li})\text{Cl}$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>11</sub>ClLiO<sub>3</sub>P**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}(\text{Li})\text{Cl}$   
 Formation: 5.5.2.3.2  
 $\text{HCCLiP}(\text{O})(\text{OC}_2\text{H}_5)_2$   
 Formation: 5.5.2.3.3
- C<sub>5</sub>H<sub>11</sub>ClMgO**  
 $\text{CH}_3\text{O}(\text{CH}_2)_4\text{MgCl}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- C<sub>5</sub>H<sub>11</sub>ClMgS**  
 $\text{C}_2\text{H}_5\text{S}(\text{CH}_2)_3\text{MgCl}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- C<sub>5</sub>H<sub>11</sub>ClSn**  
 $(\text{CH}_3)\text{ClSnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$   
 Formation: 5.7.2.3.1
- C<sub>5</sub>H<sub>11</sub>K**  
 $[\text{CH}_3(\text{CH}_2)_4]\text{K}$   
 Formation: 5.5.3.2.1, 5.5.3.2.3
- Reaction with alkanes: 5.5.3.2.3  
 $\text{K}[(\text{CH}_3)_3\text{CCH}_2]$   
 Formation: 5.5.3.2.1
- C<sub>5</sub>H<sub>11</sub>Li**  
 $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Li}$   
 Formation: 5.5.2.2.5  
 $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1, 5.5.2.2.2  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1  
 $(\text{CH}_3)_3\text{CCH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>5</sub>H<sub>11</sub>LiN<sub>2</sub>**  
 $\text{syn-LiCH}_2\text{C}(\text{CH}_3)=\text{NN}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>11</sub>LiO**  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OCH}_3)\text{Li}$   
 Formation: 5.5.2.2.5, 5.5.2.3.5
- C<sub>5</sub>H<sub>11</sub>LiOS**  
 $(\text{CH}_3)_3\text{CSOCH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>11</sub>LiOSi**  
 $(\text{Z})\text{-(CH}_3)_3\text{SiOCH}=\text{CHLi}$   
 Formation: 5.5.2.3.3
- C<sub>5</sub>H<sub>11</sub>LiO<sub>2</sub>**  
 $\text{LiCH}_2\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.1
- C<sub>5</sub>H<sub>11</sub>LiSi**  
 $\text{CH}_2=\text{C}[\text{Si}(\text{CH}_3)_3]\text{Li}$   
 Formation: 5.5.2.3.3  
 $(\text{E})\text{-(CH}_3)_3\text{SiCH}=\text{CHLi}$   
 Formation: 5.5.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>5</sub>H<sub>11</sub>Na**  
 $\text{Na}[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2]$   
 Formation: 5.5.3.2.3  
 Addition to  $\text{C}=\text{C}$ : 5.5.3.3.3  
 Base for metallation reaction: 5.5.3.3.1  
 Formation: 5.5.3.2.1  
 $\text{Na}[(\text{CH}_3)_3\text{CCH}_2]$   
 Formation: 5.5.3.2.1
- C<sub>5</sub>H<sub>12</sub>AsClMg**  
 $(\text{CH}_3)_2\text{AsCH}_2\text{CH}_2\text{CH}_2\text{MgCl}$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>5</sub>H<sub>12</sub>Se**  
 $n\text{-C}_4\text{H}_9\text{SeCH}_3$   
 Formation: 5.5.2.3.1
- C<sub>5</sub>H<sub>12</sub>Si**  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>5</sub>H<sub>13</sub>ClLiN<sub>2</sub>OP**  
 $[(\text{CH}_3)_2\text{N}]_2\text{P}(\text{O})\text{CH}(\text{Li})\text{Cl}$   
 Formation: 5.5.2.3.2



- C<sub>5</sub>H<sub>13</sub>LiOSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(OCH<sub>3</sub>)Li  
Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>13</sub>LiP<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>P]<sub>2</sub>CHLi  
Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>13</sub>LiSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(CH<sub>3</sub>)Li  
Formation: 5.5.2.2.5, 5.5.2.3.1
- C<sub>5</sub>H<sub>14</sub>Cl<sub>2</sub>Si<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>2</sub>ClSi]<sub>2</sub>CH<sub>2</sub>  
Reaction with Na-Hg: 5.7.3.2
- C<sub>5</sub>H<sub>14</sub>LiN<sub>2</sub>OP**  
[(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>P(O)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>15</sub>LiSn<sub>2</sub>**  
(CH<sub>3</sub>)<sub>3</sub>SnSn(CH<sub>3</sub>)<sub>2</sub>Li  
Formation: 5.5.6.3.1
- C<sub>5</sub>Li<sub>4</sub>**  
LiC≡CC(Li)<sub>2</sub>C≡CLi  
Formation: 5.5.2.3.2
- C<sub>6</sub>AgF<sub>5</sub>**  
C<sub>6</sub>F<sub>5</sub>Ag  
Formation: 5.6.4.2
- C<sub>6</sub>AgF<sub>13</sub>**  
AgC(CF<sub>3</sub>)<sub>2</sub>C<sub>3</sub>F<sub>7</sub>  
Formation: 5.6.4.5
- C<sub>6</sub>BrCdF<sub>5</sub>**  
C<sub>6</sub>F<sub>5</sub>CdBr  
Formation: 5.7.2.2.1
- C<sub>6</sub>BrClF<sub>4</sub>Hg**  
p-BrC<sub>6</sub>F<sub>4</sub>HgCl  
Formation: 5.7.2.3.4
- C<sub>6</sub>BrCl<sub>5</sub>Mg**  
C<sub>6</sub>Cl<sub>5</sub>MgBr  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>BrF<sub>4</sub>Li**  
o-BrC<sub>6</sub>F<sub>4</sub>Li  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>BrF<sub>5</sub>Mg**  
C<sub>6</sub>F<sub>5</sub>MgBr  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>BrF<sub>5</sub>Zn**  
C<sub>6</sub>F<sub>5</sub>ZnBr  
Formation: 5.7.2.2.1
- C<sub>6</sub>Br<sub>2</sub>F<sub>4</sub>Hg<sub>2</sub>**  
1,2-(BrHg)<sub>2</sub>C<sub>6</sub>F<sub>4</sub>  
Formation: 5.7.2.3.7
- C<sub>6</sub>Br<sub>5</sub>Li**  
C<sub>6</sub>Br<sub>5</sub>Li  
Formation: 5.5.2.3.3
- C<sub>6</sub>Br<sub>6</sub>Hg**  
C<sub>6</sub>Br<sub>5</sub>HgBr  
Formation: 5.7.2.3.2
- C<sub>6</sub>ClF<sub>5</sub>Zn**  
C<sub>6</sub>F<sub>5</sub>ZnCl  
Formation: 5.7.2.3.2
- C<sub>6</sub>Cl<sub>2</sub>F<sub>4</sub>Hg<sub>2</sub>**  
1,2-(ClHg)<sub>2</sub>C<sub>6</sub>F<sub>4</sub>  
Formation: 5.7.2.3.7
- C<sub>6</sub>Cl<sub>4</sub>Li<sub>2</sub>**  
p-LiC<sub>6</sub>Cl<sub>4</sub>Li  
Formation: 5.5.2.3.3
- C<sub>6</sub>Cl<sub>5</sub>Li**  
C<sub>6</sub>Cl<sub>5</sub>Li  
Formation: 5.5.2.3.3  
Stability: 5.5.2.3.2
- C<sub>6</sub>Cl<sub>6</sub>Hg**  
C<sub>6</sub>Cl<sub>5</sub>HgCl  
Formation: 5.7.2.3.2
- C<sub>6</sub>CuF<sub>5</sub>**  
C<sub>6</sub>F<sub>5</sub>Cu  
Formation: 5.6.4.1
- C<sub>6</sub>D<sub>5</sub>BrMg**  
C<sub>6</sub>D<sub>5</sub>MgBr  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>F<sub>5</sub>HgN<sub>3</sub>**  
C<sub>6</sub>F<sub>5</sub>HgN<sub>3</sub>  
Formation: 5.7.2.3.2
- C<sub>6</sub>F<sub>5</sub>Li**  
C<sub>6</sub>F<sub>5</sub>Li  
Formation: 5.5.2.3.3  
Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
Reaction with PbCl<sub>2</sub>: 5.5.7.5
- C<sub>6</sub>F<sub>9</sub>Li**  
CF<sub>2</sub>(CF<sub>2</sub>)<sub>3</sub>CF=CLi  
Formation: 5.5.2.3.2
- C<sub>6</sub>F<sub>14</sub>Hg**  
(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.7
- C<sub>6</sub>HCl<sub>4</sub>Li**  
2,3,4,5-Cl<sub>4</sub>C<sub>6</sub>HLi  
Formation: 5.5.2.3.2, 5.5.2.3.3
- C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>Li**  
2,3,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>2</sub>F<sub>12</sub>Hg**  
[(CF<sub>3</sub>)<sub>2</sub>CH]<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>6</sub>H<sub>2</sub>HgN<sub>4</sub>**  
[CH(CN)<sub>2</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.4
- C<sub>6</sub>H<sub>3</sub>BrCl<sub>2</sub>Hg**  
3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>HgBr  
Formation: 5.7.2.3.1

- C<sub>6</sub>H<sub>3</sub>BrCl<sub>2</sub>Mg**  
3,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>MgBr  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub>Hg**  
2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>HgCl  
Formation: 5.7.2.3.6
- C<sub>6</sub>H<sub>3</sub>LiS<sub>4</sub>**  
 $\overline{\text{SCH=CHSC=CSCH=CLiS}}$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>4</sub>BrClMg**  
p-ClC<sub>6</sub>H<sub>4</sub>MgBr  
Reaction with CdX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>H<sub>4</sub>BrHgNO<sub>2</sub>**  
m-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgBr  
Formation: 5.7.2.3.4
- C<sub>6</sub>H<sub>4</sub>BrLi**  
o-BrC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3  
p-BrC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>6</sub>H<sub>4</sub>ClCu**  
o-ClC<sub>6</sub>H<sub>4</sub>Cu  
Formation: 5.6.3
- C<sub>6</sub>H<sub>4</sub>ClHgNO<sub>2</sub>**  
m-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.4  
o-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.4, 5.7.2.3.6, 5.7.2.3.7  
p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.4
- C<sub>6</sub>H<sub>4</sub>ClLi**  
o-ClC<sub>6</sub>H<sub>4</sub>Li  
Stability: 5.5.2.3.2  
p-ClC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>Hg**  
o-ClC<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.6  
p-ClC<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.1, 5.7.2.3.6, 5.7.2.3.7
- C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>HgO<sub>2</sub>S**  
p-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>HgCl  
Desulfination: 5.7.2.3.7
- C<sub>6</sub>H<sub>4</sub>Cl<sub>3</sub>Sb**  
p-ClC<sub>6</sub>H<sub>4</sub>SbCl<sub>2</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>H<sub>4</sub>FLi**  
m-FC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3  
o-FC<sub>6</sub>H<sub>4</sub>Li  
Stability: 5.5.2.3.2  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>4</sub>HgINO<sub>2</sub>**  
p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgI  
Formation: 5.7.2.2.1
- C<sub>6</sub>H<sub>4</sub>LiNO<sub>2</sub>**  
o-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>4</sub>Li<sub>2</sub>**  
o-LiC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.2  
p-LiC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.3
- C<sub>6</sub>H<sub>4</sub>Li<sub>2</sub>O**  
o-LiOC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>4</sub>Li<sub>2</sub>O<sub>3</sub>S**  
o-LiC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>4</sub>Li<sub>2</sub>S**  
o-LiSC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>4</sub>Li<sub>3</sub>N**  
p-Li<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>5</sub>Ag**  
C<sub>6</sub>H<sub>5</sub>Ag  
Formation: 5.6.4.1
- C<sub>6</sub>H<sub>5</sub>BrCd**  
C<sub>6</sub>H<sub>5</sub>CdBr  
Formation: 5.7.2.2.1
- C<sub>6</sub>H<sub>5</sub>BrF<sub>6</sub>HgO<sub>2</sub>**  
C<sub>2</sub>H<sub>5</sub>OC(O)CF<sub>2</sub>CF(CF<sub>3</sub>)HgBr  
Formation: 5.7.2.2.1
- C<sub>6</sub>H<sub>5</sub>BrHg**  
C<sub>6</sub>H<sub>5</sub>HgBr  
Formation: 5.7.2.3.1, 5.7.2.3.6
- C<sub>6</sub>H<sub>5</sub>BrMg**  
C<sub>6</sub>H<sub>5</sub>MgBr  
Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
Reaction with Hg(CNO)<sub>2</sub>: 5.7.2.3.1  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>H<sub>5</sub>BrZn**  
C<sub>6</sub>H<sub>5</sub>ZnBr  
Formation: 5.7.2.2.1, 5.7.2.3.2
- C<sub>6</sub>H<sub>5</sub>CdI**  
C<sub>6</sub>H<sub>5</sub>CdI  
Formation: 5.7.2.3.2
- C<sub>6</sub>H<sub>5</sub>ClGe**  
C<sub>6</sub>H<sub>5</sub>GeCl  
Reaction with R<sub>2</sub>Hg: 5.7.4.8  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.8
- C<sub>6</sub>H<sub>5</sub>ClHg**  
C<sub>6</sub>H<sub>5</sub>HgCl  
Formation: 5.7.2.3.2, 5.7.2.3.6

**C<sub>6</sub>H<sub>5</sub>ClHg** *contd.*Reaction with Ar<sub>3</sub>SiLi: 5.7.3.1

Reaction with carboxylates: 5.7.2.3.7

**C<sub>6</sub>H<sub>5</sub>Cu**C<sub>6</sub>H<sub>5</sub>Cu

Formation: 5.6.4.1

Reaction with (R<sub>2</sub>P)<sub>2</sub>CH<sub>2</sub>: 5.6.4.3**C<sub>6</sub>H<sub>5</sub>F**C<sub>6</sub>H<sub>5</sub>F

Reaction with Li metal: 5.5.2.2.1

Reaction with a lithium radical aromatic anion: 5.5.2.2.1

**C<sub>6</sub>H<sub>5</sub>HgI**C<sub>6</sub>H<sub>5</sub>HgI

Formation: 5.7.2.2.1

**C<sub>6</sub>H<sub>5</sub>HgNO<sub>3</sub>**C<sub>6</sub>H<sub>5</sub>HgONO<sub>2</sub>

Formation: 5.7.2.3.2

**C<sub>6</sub>H<sub>5</sub>K**K[C<sub>6</sub>H<sub>5</sub>]Addition to C<sub>6</sub>H<sub>6</sub>: 5.5.3.3.3

Base for metallation reaction: 5.5.3.3.1

Formation: 5.5.3.2.1, 5.5.3.2.6, 5.5.3.3.1

**C<sub>6</sub>H<sub>5</sub>Li**C<sub>6</sub>H<sub>5</sub>Li

Addition to olefins: 5.5.2.3.4

Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.2.5,

5.5.2.3.3, 5.5.2.3.5

Reaction with CdX<sub>2</sub>: 5.7.2.3.1Reaction with PbCl<sub>2</sub>: 5.5.7.2.2Reaction with Ph<sub>6</sub>Pb<sub>2</sub>: 5.5.7.2.2Reaction with (R<sub>3</sub>Ge)<sub>2</sub>: 5.5.5.2.2Reaction with SnCl<sub>2</sub>: 5.5.6.6Reaction with PbCl<sub>2</sub>: 5.5.7.5

Reaction with RC≡CH: 5.5.2.3.2

Reaction with ZnX<sub>2</sub>: 5.7.2.3.1

Transmetallation: 5.5.2.3.1, 5.5.7.6

**C<sub>6</sub>H<sub>5</sub>LiNO<sub>2</sub>**[C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>

Formation: 5.5.2.2.3

**C<sub>6</sub>H<sub>5</sub>LiS**C<sub>6</sub>H<sub>5</sub>SLi

Formation: 5.5.2.2.5, 5.5.2.3.5

**C<sub>6</sub>H<sub>5</sub>LiSe**C<sub>6</sub>H<sub>5</sub>SeLi

Formation: 5.5.2.3.2

**C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>**C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>

Reaction with Li metal: 5.5.2.2.3

**C<sub>6</sub>H<sub>5</sub>Na**Na[C<sub>6</sub>H<sub>5</sub>]

Formation: 5.5.3.2.1, 5.5.3.3.2

**C<sub>6</sub>H<sub>6</sub>**C<sub>6</sub>H<sub>6</sub>

Metallation: 5.5.3.3.1

**C<sub>6</sub>H<sub>6</sub>ClHgNO<sub>2</sub>S**p-NH<sub>2</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgCl

Formation: 5.7.2.3.6

**C<sub>6</sub>H<sub>6</sub>Cs**[C<sub>6</sub>H<sub>6</sub>]<sup>-</sup>Cs<sup>+</sup>

Formation: 5.5.3.2.4

**C<sub>6</sub>H<sub>6</sub>Hg**(CH<sub>3</sub>C≡C)<sub>2</sub>Hg

Formation: 5.7.2.3.4

<sup>1</sup>H-NMR: 5.7.3**C<sub>6</sub>H<sub>6</sub>K**[C<sub>6</sub>H<sub>6</sub>]<sup>-</sup>K<sup>+</sup>

Formation: 5.5.3.2.4

**C<sub>6</sub>H<sub>6</sub>Li**[C<sub>6</sub>H<sub>6</sub>]<sup>-</sup>Li<sup>+</sup>

Formation: 5.5.2.2.3

**C<sub>6</sub>H<sub>6</sub>LiN**2-LiCH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N

Formation: 5.5.2.3.2

3-LiCH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N

Formation: 5.5.2.3.2

**C<sub>6</sub>H<sub>6</sub>Rb**[C<sub>6</sub>H<sub>6</sub>]<sup>-</sup>Rb<sup>+</sup>

Formation: 5.5.3.2.4

**C<sub>6</sub>H<sub>6</sub>Zn**(HC≡CCH<sub>2</sub>)<sub>2</sub>Zn

Formation: 5.7.2.3.1

**C<sub>6</sub>H<sub>7</sub>BO<sub>2</sub>**C<sub>6</sub>H<sub>5</sub>B(OH)<sub>2</sub>

Reaction with transition metal carbonyls: 5.7.2.3.7

**C<sub>6</sub>H<sub>7</sub>GeLi**H<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)GeLi

Formation: 5.5.5.2.1, 5.5.5.2.2

**C<sub>6</sub>H<sub>7</sub>Li**CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>LiReaction with HgX<sub>2</sub>: 5.7.2.3.1**C<sub>6</sub>H<sub>7</sub>NaSn**Na[C<sub>6</sub>H<sub>5</sub>SnH<sub>2</sub>]

Formation: 5.5.6.4

**C<sub>6</sub>H<sub>8</sub>** $\overline{\text{CH}_2\text{CH}=\text{CHCH}=\text{CHCH}_2}$ Reaction with HgX<sub>2</sub>: 5.7.2.3.3**C<sub>6</sub>H<sub>8</sub>ClLiO<sub>2</sub>**

8-chloro-3,5-dioxabicyclo[5.1.0]oct-8-yl-lithium

Formation: 5.5.2.3.3

**C<sub>6</sub>H<sub>8</sub>K<sub>2</sub>**CH<sub>2</sub>=C(CH<sub>2</sub>K)C(CH<sub>2</sub>K)=CH<sub>2</sub>

Formation: 5.5.3.3.1

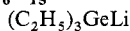
**C<sub>6</sub>H<sub>8</sub>LiNO** $\overline{\text{C}(\text{O})\text{N}(\text{CH}_3)\text{CH}(\text{CH}=\text{CH}_2)\text{CHLi}}$ 

Formation: 5.5.2.3.2

- C<sub>6</sub>H<sub>8</sub>Li<sub>2</sub>S<sub>2</sub>**  
 $[\text{CH}_2 \cdots \text{C}(\text{CH}_3) \cdots \text{CHSC}(\text{S})\text{CH}_2\text{Li}]^- \text{Li}^+$   
 Formation: 5.5.2.3.2  
 $\text{CH}_3\text{SCH}(\text{Li})\text{C}\equiv\text{CCHLiSCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>8</sub>Li<sub>3</sub>**  
 $[\text{CH}_2 \cdots \text{CH} \cdots \text{CH} - \text{CH} \cdots \text{CH} \cdots \text{C}^* \text{H}_2]^{3-} 3\text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>9</sub>ClFLiS**  
 (E)-(n-C<sub>4</sub>H<sub>9</sub>S)FC=CClLi  
 Formation: 5.5.2.3.3  
 (Z)-(n-C<sub>4</sub>H<sub>9</sub>S)FC=CClLi  
 Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>9</sub>ClHgO**  
 $\text{C}(\text{O})(\text{CH}_2)_4\text{CHHgCl}$   
 Formation: 5.7.2.3.2
- C<sub>6</sub>H<sub>9</sub>GeLi**  
 $(\text{H}_2\text{C}=\text{CH})_3\text{GeLi}$   
 Formation: 5.5.5.2.1
- C<sub>6</sub>H<sub>9</sub>Li**  
 Bicyclo[2.1.1]hex-1-yl lithium  
 Formation: 5.5.2.2.1  
 $\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)=\text{ClI}$   
 Formation: 5.5.2.3.2  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{ClI}$   
 Formation: 5.5.2.2.2  
 $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{ClI}$   
 Formation: 5.5.2.2.4  
 $\text{H}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{ClI}$   
 Formation: 5.5.2.2.1
- C<sub>6</sub>H<sub>9</sub>LiN<sub>2</sub>**  
 $\text{CHCHCHC}(\text{Li})\text{NN}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>9</sub>LiO**  
 $\text{LiCH}=\text{CHCH}=\text{CHOC}_2\text{H}_5$   
 Formation: 5.5.2.3.1  
 $\text{OC}(\text{CH}_3)=\text{CH}(\text{CH}_2)_2\text{CHLi}$   
 Formation: 5.5.2.3.5
- C<sub>6</sub>H<sub>9</sub>LiO<sub>2</sub>S**  
 $[\text{CH}_3\text{SCH} \cdots \text{CH} \cdots \text{CHCO}_2\text{CH}_3]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>9</sub>LiS**  
 $[\text{CH}_2 \cdots \text{CH} \cdots \text{CHSCH}_2 \cdots \text{CH} \cdots \text{CH}_2]^* \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>9</sub>LiS<sub>2</sub>**  
 $[\text{S}(\text{CH}_2)_3\text{SC} \cdots \text{CH} \cdots \text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>9</sub>NaPb**  
 $\text{Na}[(\text{CH}_2\text{CH})_3\text{Pb}]$   
 Formation: 5.5.7.3
- C<sub>6</sub>H<sub>9</sub>NaSn**  
 $[(\text{CH}_2=\text{CH})_3\text{Sn}]\text{Na}$   
 Formation: 5.5.6.2.2
- C<sub>6</sub>H<sub>10</sub>Br<sub>2</sub>Zn<sub>2</sub>**  
 $\text{BrZnCH}_2\text{CH}(\text{CH}_2\text{CH}=\text{CH}_2)\text{CH}_2\text{ZnBr}$   
 Formation: 5.7.2.4.2
- C<sub>6</sub>H<sub>10</sub>ClHgNO<sub>2</sub>**  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{HgCl})\text{CH}(\text{NO}_2)\text{CH}_2$   
 Formation: 5.7.2.3.3
- C<sub>6</sub>H<sub>10</sub>ClHgN<sub>3</sub>**  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{HgCl})\text{CH}(\text{N}_3)\text{CH}_2$   
 Formation: 5.7.2.3.3
- C<sub>6</sub>H<sub>10</sub>Hg**  
 $(\text{CH}_2\text{CH}_2\text{CH})_2\text{Hg}$   
 Reaction with Li metal: 5.5.2.2.2  
 $(\text{CH}_2=\text{CHCH}_2)_2\text{Hg}$   
 Reactions with Na, K, Rb or Cs metal: 5.5.3.2.3  
 $(\text{CH}_2\text{CH}_2\text{CH})_2\text{Hg}$   
 Formation: 5.7.2.3.1  
 $\text{trans}-(\text{CH}_3\text{CH}=\text{CH})_2\text{Hg}$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>6</sub>H<sub>10</sub>HgO<sub>2</sub>**  
 $[\text{CH}_3\text{C}(\text{O})\text{CH}_2]_2\text{Hg}$   
 Formation: 5.7.2.3.4
- C<sub>6</sub>H<sub>10</sub>HgO<sub>4</sub>**  
 $[\text{CH}_3\text{OC}(\text{O})\text{CH}_2]_2\text{Hg}$   
 Reaction with Hg(CN)<sub>2</sub>: 5.7.2.3.2
- C<sub>6</sub>H<sub>10</sub>LiNS<sub>2</sub>**  
 $[\text{CH}_2 \cdots \text{CH} \cdots \text{CHSC}(\text{S})\text{N}(\text{CH}_3)_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>10</sub>Li<sub>2</sub>O<sub>2</sub>**  
 $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{Li})\text{CO}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>10</sub>O**  
 $(\text{CH}_2=\text{CHCH}_2)_2\text{O}$   
 Reaction with Na or K metal: 5.5.3.2.2
- C<sub>6</sub>H<sub>10</sub>Zn**  
 $(\text{CH}_2=\text{CHCH}_2)_2\text{Zn}$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{CH}_2=\text{CHR}$ : 5.7.2.4.2  
 $(\text{cyclo-C}_3\text{H}_5)_2\text{Zn}$   
 Formation: 5.7.2.3.1
- C<sub>6</sub>H<sub>11</sub>BrLiN**  
 $[\text{HBrC} \cdots \text{CH} \cdots \text{NC}(\text{CH}_3)_3]^- \text{Li}^+$   
 Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>11</sub>BrMg**  
 $\text{cyclo-C}_6\text{H}_{11}\text{MgBr}$   
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>H<sub>11</sub>BrZn**  
 $\text{cyclo-C}_6\text{H}_{11}\text{ZnBr}$   
 Formation: 5.7.2.2.1

- C<sub>6</sub>H<sub>11</sub>ClHg**  
cyclo-C<sub>6</sub>H<sub>11</sub>HgCl  
Formation: 5.7.2.3.1, 5.7.2.3.7
- C<sub>6</sub>H<sub>11</sub>ClHgO**  
 $\text{HC}(\text{OH})\text{CH}(\text{HgCl})(\text{CH}_2)_3\text{CH}_2$   
Reaction with R<sub>2</sub>CN<sub>2</sub>: 5.7.2.3.3
- C<sub>6</sub>H<sub>11</sub>ClHgO<sub>2</sub>S**  
cyclo-C<sub>6</sub>H<sub>11</sub>SO<sub>2</sub>HgCl  
Desulfination: 5.7.2.3.7
- C<sub>6</sub>H<sub>11</sub>Cl<sub>2</sub>LiSi**  
 $(\text{CH}_3)_3\text{SiCH}_2\text{C}(\text{Li})=\text{CCl}_2$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>D<sub>2</sub>ClHg**  
threo-(CH<sub>3</sub>)<sub>3</sub>CCHDCHDHgCl  
Formation: 5.7.2.3.1
- C<sub>6</sub>H<sub>11</sub>Li**  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{Li}$   
Formation: 5.5.2.2.2  
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHLi}$   
Formation: 5.5.2.2.1, 5.5.2.2.5  
 $(\text{CH}_3)_2\text{CCH}(\text{CH}_3)\text{CHLi}$   
Formation: 5.5.2.2.1  
(cyclo-C<sub>6</sub>H<sub>11</sub>)Li  
Formation: 5.5.2.3.5  
 $[\text{C}_2\text{H}_5\text{CH}\cdots\text{C}(\text{CH}_3)\cdots\text{CH}_2]^- \text{Li}^+$   
Formation: 5.5.2.3.1
- C<sub>6</sub>H<sub>11</sub>LiNO<sub>3</sub>P**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}(\text{Li})\text{CN}$   
Formation: 5.5.2.3.2  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}(\text{Li})\text{NC}$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>LiN<sub>2</sub>**  
 $(\text{C}_2\text{H}_5)_2\text{NCH}(\text{Li})\text{CN}$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>LiOS<sub>2</sub>**  
(E)-C<sub>2</sub>H<sub>5</sub>SCH=CLiS(O)C<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2  
(Z)-C<sub>2</sub>H<sub>5</sub>SCH=CLiS(O)C<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2  
(Z)-C<sub>2</sub>H<sub>5</sub>SC(Li)=CHS(O)C<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>LiO<sub>2</sub>**  
LiCH<sub>2</sub>CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>LiO<sub>2</sub>S**  
LiCH<sub>2</sub>CO[=S(CH<sub>3</sub>)<sub>2</sub>]COCH<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>LiS<sub>2</sub>**  
(Z)-C<sub>2</sub>H<sub>5</sub>SC(Li)=CHSC<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>11</sub>LiSi**  
 $(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_2\text{Li}$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>12</sub>BrNOZn**  
BrZnCH<sub>2</sub>CON(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.7.2.2.1
- C<sub>6</sub>H<sub>12</sub>Br<sub>2</sub>Hg<sub>2</sub>O**  
O[(CH<sub>2</sub>)<sub>3</sub>HgBr]<sub>2</sub>  
Formation: 5.7.2.3.3
- C<sub>6</sub>H<sub>12</sub>CLiSi**  
 $[(\text{CH}_3)_3\text{SiCCl}\cdots\text{CH}\cdots\text{CH}_2]^- \text{Li}^+$   
Formation: 5.5.2.3.1
- C<sub>6</sub>H<sub>12</sub>Cl<sub>2</sub>Hg<sub>2</sub>O<sub>2</sub>**  
[ClHgCH<sub>2</sub>CH(CH<sub>3</sub>)O]<sub>2</sub>  
Formation: 5.7.2.3.3
- C<sub>6</sub>H<sub>12</sub>CsN**  
Cs[cyclo-C<sub>6</sub>H<sub>11</sub>NH]  
Base for metallation reaction: 5.5.3.3.1
- C<sub>6</sub>H<sub>12</sub>F<sub>2</sub>Sn**  
 $(\text{CH}_3)_3\text{SnCH}_2\text{CH}=\text{CF}_2$   
Transmetallation: 5.5.2.3.1
- C<sub>6</sub>H<sub>12</sub>HgSi**  
 $(\text{CH}_3)_3\text{SiHgC}\equiv\text{CCH}_3$   
<sup>1</sup>H-NMR: 5.7.3
- C<sub>6</sub>H<sub>12</sub>LiN**  
 $\text{CH}_2=\text{C}(\text{CH}_2\text{Li})\text{CH}_2\text{N}(\text{CH}_3)_2$   
Formation: 5.5.2.3.2  
LiCH<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>  
Formation: 5.5.2.3.1
- C<sub>6</sub>H<sub>12</sub>LiNO<sub>2</sub>**  
 $(\text{CH}_3)_2\text{NCH}_2\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>12</sub>LiO<sub>4</sub>P**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\overline{\text{C}(\text{Li})\text{CH}_2\text{O}}$   
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>12</sub>Li<sub>2</sub>**  
LiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.1
- C<sub>6</sub>H<sub>12</sub>Li<sub>2</sub>O**  
LiCH<sub>2</sub>CH[CH(CH<sub>3</sub>)<sub>2</sub>]CH<sub>2</sub>OLi  
Formation: 5.5.2.3.4  
O(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Li)<sub>2</sub>  
Formation: 5.5.2.2.5, 5.5.2.3.5
- C<sub>6</sub>H<sub>12</sub>S<sub>4</sub>**  
1,1-(CH<sub>3</sub>S)<sub>2</sub> $\overline{\text{CS}(\text{CH}_2)_3\text{S}}$   
Transmetallation: 5.5.2.3.1
- C<sub>6</sub>H<sub>12</sub>Sn**  
 $(\text{CH}_3)_3\text{SnCH}=\text{C}=\text{CH}_2$   
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>6</sub>H<sub>13</sub>ClHg**  
C<sub>6</sub>H<sub>13</sub>HgCl  
Formation: 5.7.2.3.7  
n-C<sub>6</sub>H<sub>13</sub>HgCl  
Formation: 5.7.2.3.1
- C<sub>6</sub>H<sub>13</sub>ClHgO<sub>2</sub>S**  
C<sub>6</sub>H<sub>13</sub>SO<sub>2</sub>HgCl  
Desulfination: 5.7.2.3.7

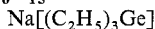
- C<sub>6</sub>H<sub>13</sub>Li**  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1  
 $(\text{CH}_3\text{CH}_2)_2\text{CHCH}_2\text{Li}$   
 Formation: 5.5.2.2.1  
 $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.2.5
- C<sub>6</sub>H<sub>13</sub>LiN<sub>2</sub>**  
 $[\text{CH}_2=\text{C}(\text{CH}_2\text{CH}_3)=\text{NN}(\text{CH}_3)_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>13</sub>LiOSi**  
 $[\text{CH}_2\vdots\text{CH}\vdots\text{CHOSi}(\text{CH}_3)_3]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>13</sub>LiO<sub>2</sub>**  
 $\text{LiCH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.1
- C<sub>6</sub>H<sub>13</sub>LiSi**  
 $[(\text{CH}_3)_3\text{SiCH}\vdots\text{CH}\vdots\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2  
 $(\text{CH}_3)_3\text{Si}\overline{\text{C}}(\text{Li})\text{CH}_2\text{CH}_2$   
 Formation: 5.5.2.2.5  
 $1\text{-Li-1-}(\text{CH}_3)_3\text{Si}\overline{\text{C}}\text{CH}_2\text{CH}_2$   
 Formation: 5.5.2.3.1
- C<sub>6</sub>H<sub>13</sub>NaO**  
 $\text{Na}[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}]$   
 Reagent for metal-metal exchange:  
 5.5.3.3.2
- C<sub>6</sub>H<sub>14</sub>Cd**  
 $(n\text{-C}_3\text{H}_7)_2\text{Cd}$   
 Reaction with  $\text{CdX}_2$ : 5.7.2.3.2
- C<sub>6</sub>H<sub>14</sub>ClHgN**  
 $(\text{CH}_3)_2\text{NCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{HgCl}$   
 Formation: 5.7.2.3.3
- C<sub>6</sub>H<sub>14</sub>Cl<sub>2</sub>HgSn**  
 $(\text{CH}_3)_2\text{ClSn}(\text{CH}_3)_4\text{HgCl}$   
 Formation: 5.7.2.3.1
- C<sub>6</sub>H<sub>14</sub>CsN**  
 $\text{Cs}[(i\text{-C}_3\text{H}_7)_2\text{N}]$   
 Base for metallation reaction: 5.5.3.3.1
- C<sub>6</sub>H<sub>14</sub>Hg**  
 $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Hg}$   
 Formation: 5.7.2.2.1  
 Reaction with Li metal: 5.5.2.2.2  
 $(i\text{-C}_3\text{H}_7)_2\text{Hg}$   
 Formation: 5.7.2.3.1  
 Reaction with Zn metal: 5.7.2.2.2
- C<sub>6</sub>H<sub>14</sub>KN**  
 $\text{K}[(i\text{-C}_3\text{H}_7)_2\text{N}]$   
 Base for metallation reaction: 5.5.3.3.1
- C<sub>6</sub>H<sub>14</sub>LiNS**  
 $(\text{CH}_3)_3\text{C}(\text{S})\text{N}(\text{CH}_3)\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>14</sub>LiO<sub>3</sub>PS**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}(\text{Li})\text{SCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>14</sub>LiO<sub>5</sub>PS**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CHLiSO}_2\text{CH}_3$   
 Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>14</sub>NNa**  
 $\text{Na}[(i\text{-C}_3\text{H}_7)_2\text{N}]$   
 Base for metallation reaction: 5.5.3.3.1
- C<sub>6</sub>H<sub>14</sub>Na<sub>2</sub>Sn**  
 $\text{Na}_2[(i\text{-C}_3\text{H}_7)_2\text{Sn}]$   
 Formation: 5.5.6.2.2
- C<sub>6</sub>H<sub>14</sub>Sn**  
 $\text{CH}_3\text{CH}=\text{CHSn}(\text{CH}_3)_3$   
 Reaction with Li metal: 5.5.2.2.2  
 $(\text{CH}_3)_2\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>6</sub>H<sub>14</sub>Zn**  
 $(i\text{-C}_3\text{H}_7)_2\text{Zn}$   
 Formation: 5.7.2.2.2
- C<sub>6</sub>H<sub>15</sub>Al**  
 $(\text{C}_2\text{H}_5)_3\text{Al}$   
 Reaction with  $\text{CdX}_2$ : 5.7.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>6</sub>H<sub>15</sub>AsHg<sub>3</sub>O<sub>4</sub>**  
 $(\text{C}_2\text{H}_5\text{HgO})_3\text{AsO}$   
 Formation: 5.7.2.3.2
- C<sub>6</sub>H<sub>15</sub>Bi**  
 $(\text{C}_2\text{H}_5)_3\text{Bi}$   
 Formation: 5.7.4.4
- C<sub>6</sub>H<sub>15</sub>BrGe**  
 $(\text{C}_2\text{H}_5)_3\text{GeBr}$   
 Formation: 5.7.4.6, 5.7.5.3
- C<sub>6</sub>H<sub>15</sub>BrSn**  
 $(\text{C}_2\text{H}_5)_3\text{SnBr}$   
 Reaction with Na metal: 5.5.6.3.2
- C<sub>6</sub>H<sub>15</sub>ClGe**  
 $(\text{C}_2\text{H}_5)_3\text{GeCl}$   
 Formation: 5.7.4.5
- C<sub>6</sub>H<sub>15</sub>ClSn**  
 $(\text{C}_2\text{H}_5)_3\text{SnCl}$   
 Reaction with Na metal: 5.5.6.3.2
- C<sub>6</sub>H<sub>15</sub>CsGe**  
 $\text{Cs}[(\text{C}_2\text{H}_5)_3\text{Ge}]$   
 Formation: 5.5.5.7
- C<sub>6</sub>H<sub>15</sub>CsSi**  
 $\text{Cs}[(\text{C}_2\text{H}_5)_3\text{Si}]$   
 Formation: 5.5.4.7
- C<sub>6</sub>H<sub>15</sub>GeK**  
 $\text{K}[(\text{C}_2\text{H}_5)_3\text{Ge}]$   
 Formation: 5.5.5.7  
 Reaction with Cs metal: 5.5.5.7  
 Formation: 5.5.3.3.3, 5.5.5.2.1, 5.5.5.2.2

**C<sub>6</sub>H<sub>15</sub>GeLi**

Formation: 5.5.5.2.2, 5.5.5.6

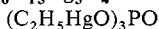
Reaction with KF, RbF or CsF: 5.5.5.7

Reaction with Cs metal: 5.5.5.7

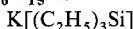
**C<sub>6</sub>H<sub>15</sub>GeNa**

Formation: 5.5.5.6

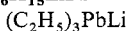
Reaction with Na metal: 5.5.5.7

**C<sub>6</sub>H<sub>15</sub>Hg<sub>3</sub>O<sub>4</sub>P**

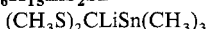
Formation: 5.7.2.3.2

**C<sub>6</sub>H<sub>15</sub>KSi**

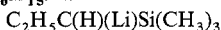
Formation: 5.5.4.6, 5.5.4.7

**C<sub>6</sub>H<sub>15</sub>LiPb**

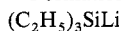
Formation: 5.5.7.4

**C<sub>6</sub>H<sub>15</sub>LiS<sub>2</sub>Sn**

Formation: 5.5.2.3.2

**C<sub>6</sub>H<sub>15</sub>LiSi**

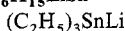
Formation: 5.5.2.3.5



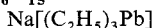
Formation: 5.5.3.3.3, 5.5.4.2.1, 5.5.4.4, 5.5.4.6

Reaction with MF: 5.5.4.7

Reaction with K metal: 5.5.4.7

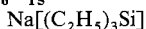
**C<sub>6</sub>H<sub>15</sub>LiSn**

Formation: 5.5.6.3.1

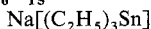
**C<sub>6</sub>H<sub>15</sub>NaPb**

Formation: 5.5.7.3, 5.5.7.4

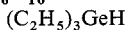
Intermediate: 5.5.7.6

**C<sub>6</sub>H<sub>15</sub>NaSi**

Formation: 5.5.4.6

**C<sub>6</sub>H<sub>15</sub>NaSn**

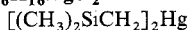
Formation: 5.5.6.2.2, 5.5.6.3.2

**C<sub>6</sub>H<sub>16</sub>Ge**

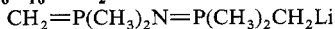
Formation: 5.5.5.2.2

Reaction with R<sub>2</sub>Cd: 5.7.4.2Reaction with R<sub>2</sub>Hg: 5.7.4.2

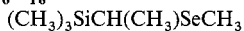
Reaction with Zn metal: 5.7.4.2

**C<sub>6</sub>H<sub>16</sub>HgSi<sub>2</sub>**

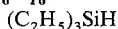
Thermal stability: 5.7.5

**C<sub>6</sub>H<sub>16</sub>LiNP<sub>2</sub>**

Formation: 5.5.2.3.2

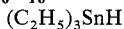
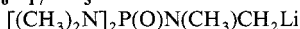
**C<sub>6</sub>H<sub>16</sub>SeSi**

Transmetallation: 5.5.2.3.1

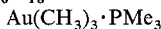
**C<sub>6</sub>H<sub>16</sub>Si**Reaction with R<sub>2</sub>Zn, R<sub>2</sub>Cd or R<sub>2</sub>Hg: 5.7.3.3

Reaction with Na-K: 5.5.4.4

Reaction with NaH or KH: 5.5.4.4

**C<sub>6</sub>H<sub>16</sub>Sn**Reaction with R<sub>2</sub>Hg: 5.7.5.2.3Reaction with R<sub>2</sub>Zn: 5.7.5.2.1**C<sub>6</sub>H<sub>17</sub>LiN<sub>3</sub>OP**

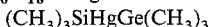
Formation: 5.5.2.3.2

**C<sub>6</sub>H<sub>18</sub>AuP**

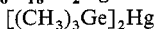
Formation: 5.6.4.1

**C<sub>6</sub>H<sub>18</sub>BLiP<sub>2</sub>**

Formation: 5.5.2.3.2

**C<sub>6</sub>H<sub>18</sub>GeHgSi**

Formation: 5.7.3.5

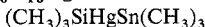
**C<sub>6</sub>H<sub>18</sub>Ge<sub>2</sub>Hg**

Formation: 5.7.3.5, 5.7.4.3

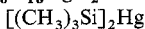
Reaction with AuX: 5.6.5.3

Reaction with H<sub>3</sub>GeX: 5.7.4, 5.7.4.7Reaction with (R<sub>3</sub>Si)<sub>2</sub>Hg: 5.7.3.5

Reaction with Li metal: 5.5.5.6

<sup>1</sup>H-NMR: 5.7.3**C<sub>6</sub>H<sub>18</sub>HgSiSn**

Formation: 5.7.3.5

**C<sub>6</sub>H<sub>18</sub>HgSi<sub>2</sub>**

Decomposition: 5.7.3

Formation: 5.7.3.2

Reactions with organotin alkoxides: 5.7.5.4

Reaction with GeX<sub>4</sub>: 5.7.4.7Reaction with R<sub>3</sub>GeOR: 5.7.3.5Reaction with R<sub>3</sub>SiLi: 5.7.3.1Reaction with R<sub>3</sub>SnX: 5.7.5.4Reaction with R<sub>3</sub>SnOR: 5.7.3.5Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.3.5Reaction with SiX<sub>4</sub>: 5.7.3.3Reaction with H<sub>3</sub>SiX: 5.7.3

Reaction with Li metal: 5.5.4.6

Reaction with group-IA metals: 5.7.3.1

<sup>1</sup>H-NMR: 5.7.3

- C<sub>6</sub>H<sub>18</sub>HgSn<sub>2</sub>**  
 [(CH<sub>3</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
 Formation: 5.7.5.2.3, 5.7.5.4
- C<sub>6</sub>H<sub>18</sub>NNaSi<sub>2</sub>**  
 Na[[[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>N]  
 Base for metallation reaction: 5.5.3.3.1
- C<sub>6</sub>H<sub>18</sub>O<sub>2</sub>Si<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>O)<sub>2</sub>SiSi(CH<sub>3</sub>O)(CH<sub>3</sub>)<sub>2</sub>  
 Reaction with NaOR: 5.5.4.2.2
- C<sub>6</sub>H<sub>18</sub>O<sub>4</sub>Si<sub>2</sub>**  
 CH<sub>3</sub>(CH<sub>3</sub>O)<sub>2</sub>SiSi(CH<sub>3</sub>O)<sub>2</sub>CH<sub>3</sub>  
 Reaction with NaOR: 5.5.4.2.2
- C<sub>6</sub>H<sub>18</sub>Pb<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>3</sub>PbPb(CH<sub>3</sub>)<sub>3</sub>  
 Reaction with RHgX: 5.7.6.2
- C<sub>6</sub>H<sub>18</sub>Si<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>3</sub>SiSi(CH<sub>3</sub>)<sub>3</sub>  
 Formation: 5.7.3, 5.7.3.2, 5.7.4.7  
 Reaction with RLi: 5.5.4.2.2  
 Reaction with KOR: 5.5.4.2.2  
 Reaction with Li metal: 5.5.4.2.1
- C<sub>6</sub>H<sub>18</sub>Sn<sub>2</sub>**  
 (CH<sub>3</sub>)<sub>3</sub>SnSn(CH<sub>3</sub>)<sub>3</sub>  
 Reaction with RLi: 5.5.6  
 Reaction with NaNH<sub>2</sub>: 5.5.6  
 Reaction with Li: 5.5.6.2.1  
 Reaction with Na-K: 5.5.6.2.3  
 Reaction with Na or Na naphthalene:  
 5.5.6.2.2
- C<sub>6</sub>H<sub>19</sub>NSi<sub>2</sub>**  
 HN[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>  
 Formation: 5.7.2.3.4
- C<sub>6</sub>H<sub>21</sub>LiSi<sub>4</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>HSi]<sub>3</sub>SiLi  
 Formation: 5.5.4.2.2
- C<sub>6</sub>Li**  
 LiC<sub>6</sub>  
 Formation: 5.5.2.1
- C<sub>7</sub>BrCl<sub>6</sub>Li**  
 ClCICl=CCICl(CCl<sub>2</sub>)CBr=Cl  
 Formation: 5.5.2.3.3
- C<sub>7</sub>CuF<sub>15</sub>**  
 C<sub>7</sub>F<sub>15</sub>Cu  
 Formation: 5.6.3
- C<sub>7</sub>F<sub>5</sub>HgN**  
 C<sub>6</sub>F<sub>5</sub>HgCN  
 Formation: 5.7.2.3.2
- C<sub>7</sub>F<sub>15</sub>Li**  
 CF<sub>3</sub>(CF<sub>2</sub>)<sub>6</sub>Li  
 Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>3</sub>ClF<sub>4</sub>HgO**  
 p-CH<sub>3</sub>OC<sub>6</sub>F<sub>4</sub>HgCl  
 Formation: 5.7.2.3.4
- C<sub>7</sub>H<sub>3</sub>ClLiN**  
 2-Li-3-CNC<sub>6</sub>H<sub>3</sub>Cl  
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>3</sub>-3-NCC<sub>6</sub>H<sub>3</sub>Cl**  
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>3</sub>Cl<sub>2</sub>F<sub>3</sub>Hg<sub>2</sub>**  
 3,5-(ClHg)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CF<sub>3</sub>  
 Formation: 5.7.2.3.4
- C<sub>7</sub>H<sub>3</sub>F<sub>5</sub>Hg**  
 CH<sub>3</sub>HgC<sub>6</sub>F<sub>5</sub>  
 Formation: 5.7.2.3.7
- C<sub>7</sub>H<sub>4</sub>ClF<sub>3</sub>Hg**  
 m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
 Formation: 5.7.2.3.4
- C<sub>7</sub>H<sub>4</sub>CuF<sub>3</sub>**  
 m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
 Reaction with RBr: 5.6.4.2
- C<sub>7</sub>H<sub>4</sub>F<sub>3</sub>Li**  
 m-LiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>  
 Formation: 5.5.2.3.2  
 n-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li  
 Formation: 5.5.2.3.3  
 o-LiC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>  
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>4</sub>LiN**  
 m-NCC<sub>6</sub>H<sub>4</sub>Li  
 Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>4</sub>Li<sub>2</sub>O<sub>2</sub>**  
 o-LiC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Li  
 Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>5</sub>Br<sub>2</sub>Li**  
 C<sub>6</sub>H<sub>5</sub>CBr<sub>2</sub>Li  
 Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>5</sub>Cl<sub>2</sub>Li**  
 C<sub>6</sub>H<sub>5</sub>CCl<sub>2</sub>Li  
 Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>5</sub>Cl<sub>3</sub>Hg**  
 C<sub>6</sub>H<sub>5</sub>HgCCl<sub>3</sub>  
 Formation: 5.7.2.3.7
- C<sub>7</sub>H<sub>5</sub>HgNO**  
 C<sub>6</sub>H<sub>5</sub>HgCNO  
 Formation: 5.7.2.3.1
- C<sub>7</sub>H<sub>5</sub>LiS<sub>2</sub>**  
 o-C<sub>6</sub>H<sub>4</sub>SCH(Li)S  
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>5</sub>Li<sub>3</sub>O<sub>2</sub>S**  
 C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>CLi<sub>3</sub>  
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>ClLiOS**  
 C<sub>6</sub>H<sub>5</sub>SOCHLiCl  
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>Cl<sub>2</sub>Mg**  
 o-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>MgCl  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1



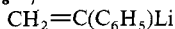
- C<sub>7</sub>H<sub>6</sub>FLi**  
2-F-5-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>FLiO**  
2-Li-3-CH<sub>3</sub>OC<sub>6</sub>H<sub>3</sub>F  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>LiNO<sub>2</sub>**  
4-CH<sub>3</sub>-2-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>6</sub>Li<sub>2</sub>**  
m-LiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>Li<sub>2</sub>O**  
o-LiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OLi  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>Li<sub>2</sub>O<sub>2</sub>S**  
C<sub>6</sub>H<sub>5</sub>S(O)<sub>2</sub>CHLi<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>6</sub>Li<sub>2</sub>S**  
C<sub>6</sub>H<sub>5</sub>CH(Li)SLi  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>7</sub>BrHg**  
o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>HgBr  
Formation: 5.7.2.3.7
- C<sub>7</sub>H<sub>7</sub>BrHgO**  
m-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>HgBr  
Formation: 5.7.2.3.7
- C<sub>7</sub>H<sub>7</sub>BrMg**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>MgBr  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>7</sub>H<sub>7</sub>BrZn**  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>ZnBr  
Formation: 5.7.2.3.2
- C<sub>7</sub>H<sub>7</sub>ClHg**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>HgCl  
Formation: 5.7.2.3.1  
o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.2.3  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.7
- C<sub>7</sub>H<sub>7</sub>ClHgO<sub>2</sub>S**  
C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>CH<sub>2</sub>HgCl  
Formation: 5.7.2.3.2
- C<sub>7</sub>H<sub>7</sub>ClMg**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>MgCl  
Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
Reaction with Li metal: 5.5.2.2.2
- C<sub>7</sub>H<sub>7</sub>ClZn**  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>ZnCl  
Formation: 5.7.2.3.2
- C<sub>7</sub>H<sub>7</sub>Cl<sub>4</sub>NSi**  
(p-C<sub>6</sub>Cl<sub>4</sub>N)Si(CH<sub>3</sub>)<sub>2</sub>H  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>7</sub>Cs**  
Cs[C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>]  
Formation: 5.5.3.2.5, 5.5.3.2.6, 5.5.3.3.1
- C<sub>7</sub>H<sub>7</sub>Cu**  
4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Cu  
Reaction with RH: 5.6.4.3
- C<sub>7</sub>H<sub>7</sub>CuO**  
2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>Cu  
Formation: 5.6.4.1
- C<sub>7</sub>H<sub>7</sub>HgI**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>HgI  
Formation: 5.7.2.2.1  
Reaction with R<sub>2</sub>CN<sub>2</sub>: 5.7.2.3.3
- C<sub>7</sub>H<sub>7</sub>IZn**  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>ZnI  
Formation: 5.7.2.3.2
- C<sub>7</sub>H<sub>7</sub>K**  
K[C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>]  
Formation: 5.5.3.2.2, 5.5.3.2.5, 5.5.3.2.6, 5.5.3.3.1
- C<sub>7</sub>H<sub>7</sub>Li**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.2, 5.5.2.2.5, 5.5.2.3.1, 5.5.2.3.2  
m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.1  
o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.1  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.3.1  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>7</sub>LiN<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>N=NCH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>7</sub>LiO**  
o-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.2  
p-(CH<sub>3</sub>O)C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1
- C<sub>7</sub>H<sub>7</sub>LiOS**  
C<sub>6</sub>H<sub>5</sub>SOCH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>7</sub>LiOSe**  
C<sub>6</sub>H<sub>5</sub>Se(O)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>7</sub>LiO<sub>2</sub>S**  
C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>CH<sub>2</sub>Li  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>7</sub>H<sub>7</sub>LiS**  
C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>Li  
Formation: 5.5.2.2.2, 5.5.2.2.5, 5.5.2.3.2, 5.5.2.3.3

- Reaction with  $\text{HgX}_2$ : 5.7.2.3.1  
 $\text{o-LiC}_6\text{H}_4\text{SCH}_3$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_7\text{LiSe}$**   
 $\text{C}_6\text{H}_5\text{SeCH}_2\text{Li}$   
 Formation: 5.5.2.3.1, 5.5.2.3.2, 5.5.2.3.3
- $\text{C}_7\text{H}_7\text{LiTe}$**   
 $\text{C}_6\text{H}_5\text{TeCH}_2\text{Li}$   
 Formation: 5.5.2.3.1
- $\text{C}_7\text{H}_7\text{Li}_3$**   
 $[\text{CH}\cdots\text{CH}\cdots\text{CH}\cdots\text{CH}\cdots\text{CH}\cdots\text{CH}\cdots\text{C}^*\text{H}]^3-3\text{Li}^+$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_7\text{Na}$**   
 $\text{Na}[\text{C}_6\text{H}_5\text{CH}_2]$   
 Formation: 5.5.3.2.3, 5.5.3.3.1  
 Reaction with THF: 5.5.3.2.3
- $\text{C}_7\text{H}_8\text{ClLi}$**   
 $\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_2)\text{CCl}=\text{CLi}$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_8\text{O}$**   
 $\text{C}_6\text{H}_5\text{OCH}_3$   
 Reaction with K metal: 5.5.3.2.2
- $\text{C}_7\text{H}_8\text{S}$**   
 $\text{C}_6\text{H}_5\text{SCH}_3$   
 Reaction with K metal: 5.5.3.2.2
- $\text{C}_7\text{H}_8\text{Se}$**   
 $\text{C}_6\text{H}_5\text{SeCH}_3$   
 Transmetallation: 5.5.2.3.1
- $\text{C}_7\text{H}_9\text{LiN}_2$**   
 $\text{CH}_2(\text{CH}_2)_3\text{NCH}=\text{CLiCN}$   
 Formation: 5.5.2.3.2  
 $\text{CH}_2(\text{CH}_2)_3\text{NCLi}=\text{CHCN}$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_9\text{LiOS}$**   
 $\text{CH}_3\text{SC}(\text{CH}_3)\text{C}=\text{C}=\text{CLiOCH}_3$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_9\text{Li}_3$**   
 $[(\text{CH}_2\cdots)_2\text{C}\cdots\text{CH}\cdots\text{C}(\cdots\text{CH}_2)_2]^3-3\text{Li}^+$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_9\text{Na}$**   
 $\text{C}(\text{Na})\text{CH}_2\text{CHCH}_2\text{CHCHCH}_2$   
 Formation: 5.5.3.3.1
- $\text{C}_7\text{H}_{10}\text{Li}_2$**   
 1,4-Dilithiobicyclo[2.2.1]heptane  
 Formation: 5.5.2.2.1
- $\text{C}_7\text{H}_{11}\text{Li}$**   
 $\text{H}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CLi}$   
 Formation: 5.5.2.2.1  
 $\text{n-C}_4\text{H}_9\text{CH}_2\text{C}\equiv\text{CLi}$   
 Formation: 5.5.2.3.3
- 7-Lithiobicyclo[4.1.0]heptane  
 Formation: 5.5.2.2.1
- 7-Lithionorbornane  
 Formation: 5.5.2.2.1
- $\text{C}_7\text{H}_{11}\text{LiN}_2$**   
 $\text{C}(\text{CH}_3)\text{CHClLiN}(\text{C}_3\text{H}_7\text{-i})$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_{11}\text{LiO}_2$**   
 $[\text{CH}_2\text{OC}(\text{CH}_3)_2\text{OCH}\cdots\text{C}\cdots\text{CH}_2]\text{Li}$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_{12}\text{HgO}_2$**   
 $(\text{E})\text{-(C}_3\text{H}_7\text{CH}=\text{CH})\text{HgOC}(\text{O})\text{CH}_3$   
 Formation: 5.7.2.3.1
- $\text{C}_7\text{H}_{12}\text{HgO}_2\text{Si}$**   
 $(\text{CH}_3)_3\text{SiC}\equiv\text{CHgOC}(\text{O})\text{CH}_3$   
 Formation: 5.7.2.3.4
- $\text{C}_7\text{H}_{12}\text{HgO}_3$**   
 $\text{CH}_3\text{C}(\text{O})\text{OHgCH}(\text{CH}_2)_2\text{CH}(\text{OH})\text{CH}_2$   
 Formation: 5.7.2.3.3
- $\text{C}_7\text{H}_{12}\text{HgO}_4$**   
 $\text{CH}_3\text{CH}(\text{OAc})\text{CH}_2\text{HgOAc}$   
 Reaction with  $\beta$ -diketones: 5.7.2.3.3
- $\text{C}_7\text{H}_{12}\text{LiN}$**   
 $[(\text{CH}_3)_3\text{CNCH}\cdots\text{C}\cdots\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2  
 $\text{LiCH}_2\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$   
 Formation: 5.5.2.3.2  
 $[\text{N}(\text{CH}_2)_3\text{CH}_2\text{CH}\cdots\text{CH}\cdots\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_{12}\text{LiNOS}$**   
 $[\text{CH}_3\text{CH}\cdots\text{CH}\cdots\text{CHSC}(\text{O})\text{N}(\text{CH}_3)_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_{12}\text{LiNOS}_2$**   
 $[\text{CH}_2\cdots\text{C}(\text{OCH}_3)\cdots\text{CHSC}(\text{S})\text{N}(\text{CH}_3)_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_{12}\text{Sn}$**   
 $(\text{CH}_3)_2\text{SnCH}=\text{CHCH}_2\text{CH}=\text{CH}$   
 Reaction with  $\text{RLi}$ : 5.5.2.3.1
- $\text{C}_7\text{H}_{13}\text{B}_2\text{LiO}_4$**   
 $\text{CHLi}[\text{BO}(\text{CH}_2)_3\text{O}]_2$   
 Formation: 5.5.2.3.2
- $\text{C}_7\text{H}_{13}\text{BrHg}$**   
 $\text{cis-3-CH}_3\text{-cyclo-C}_6\text{H}_{10}\text{HgBr}$   
 Formation: 5.7.2.3.1
- $\text{C}_7\text{H}_{13}\text{ClHgO}$**   
 $\text{HC}(\text{OH})\text{CH}(\text{HgCH}_2\text{Cl})(\text{CH}_2)_3\text{CH}_2$   
 Formation: 5.7.2.3.3
- $\text{C}_7\text{H}_{13}\text{ClMg}$**   
 $\text{cis-3-CH}_3\text{-cyclo-C}_6\text{H}_{10}\text{MgCl}$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1

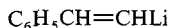
- C<sub>7</sub>H<sub>13</sub>Li**  
 $\overline{\text{CH}_2(\text{CH}_2)_4\text{CHCH}_2\text{Li}}$   
 Formation: 5.5.2.3.4  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{Li}$   
 Formation: 5.5.2.2.5  
 $(\text{CH}_3)_2\overline{\text{CC}(\text{CH}_3)_2\text{CHLi}}$   
 Formation: 5.5.2.2.1  
 $(\text{CH}_3)_3\text{CCH}=\text{CHCH}_2\text{Li}$   
 Substrate in metal-metal exchange:  
 5.5.3.3.2  
 (E)-n-C<sub>3</sub>H<sub>7</sub>(Li)C=CHC<sub>2</sub>H<sub>5</sub>  
 Formation: 5.5.2.3.3  
 (Z)-n-C<sub>3</sub>H<sub>7</sub>(Li)C=CHC<sub>2</sub>H<sub>5</sub>  
 Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>13</sub>LiO**  
 $\text{CH}_2=\text{CHOCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>7</sub>H<sub>13</sub>Li<sub>2</sub>N**  
 $\text{CH}(\text{Li})=\text{CHCH}_2\text{NLi}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>13</sub>Na**  
 $\text{Na}[(\text{CH}_3)_3\text{CCH}=\text{CHCH}_2]$   
 Formation: 5.5.3.3.2
- C<sub>7</sub>H<sub>14</sub>LiNO**  
 $\text{LiC}(\text{O})\text{N}(\text{i-C}_3\text{H}_7)_2$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>14</sub>LiNOSi**  
 $(\text{CH}_3)_3\text{SiO}(\text{CH}_2)_2\text{CH}(\text{CN})\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>14</sub>LiNS**  
 $(\text{CH}_3)_3\text{CC}(\text{S})\text{N}(\text{CH}_3)\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>14</sub>LiO<sub>4</sub>P**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CHOP}(\text{O})(\text{OC}_2\text{H}_5)_2]^{-}\text{Li}^{+}$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>14</sub>LiO<sub>5</sub>P**  
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}(\text{Li})\text{CO}_2\text{CH}_3$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>14</sub>Li<sub>2</sub>O**  
 $\text{LiCH}_2\text{CH}[\text{C}(\text{CH}_3)_3]\text{CH}_2\text{OLi}$   
 Formation: 5.5.2.3.4  
 $\text{LiCH}_2\text{CH}[(\text{CH}_2)_3\text{CH}_3]\text{CH}_2\text{OLi}$   
 Formation: 5.5.2.3.4
- C<sub>7</sub>H<sub>15</sub>BrHgO<sub>2</sub>**  
 $(\text{CH}_3)_3\text{COO}(\text{CH}_2)_3\text{HgBr}$   
 Formation: 5.7.2.3.3
- C<sub>7</sub>H<sub>15</sub>GeLiOS**  
 $(\text{CH}_3)_3\text{GeC}(\text{Li})\overline{\text{O}(\text{CH}_2)_3\text{S}}$   
 Formation: 5.2.3.1, 5.5.2.3.1, 5.5.2.3.2
- C<sub>7</sub>H<sub>15</sub>Li**  
 $\text{CH}_3\text{CH}[\text{C}(\text{CH}_3)_3]\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.4
- $\text{CH}_3\text{CH}(\text{Li})\text{CH}_2\text{C}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.4  
 $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.2.5  
 $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.5, 5.5.2.3.5
- C<sub>7</sub>H<sub>15</sub>LiOS**  
 $(\text{CH}_3)_3\text{CSOC}(\text{Li})(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>15</sub>LiOSSI**  
 $(\text{CH}_3)_3\text{SiCH}(\text{Li})\text{C}(\text{S})\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.2  
 $(\text{CH}_3)_3\text{Si}\overline{\text{C}(\text{Li})\text{O}(\text{CH}_2)_3\text{S}}$   
 Formation: 5.5.2.3.1, 5.5.2.3.2
- C<sub>7</sub>H<sub>15</sub>LiOSi**  
 $\text{LiCH}_2\text{CH}=\text{C}(\text{CH}_3)[\text{OSi}(\text{CH}_3)_3]$   
 Formation: 5.5.2.3.5
- C<sub>7</sub>H<sub>15</sub>LiO<sub>2</sub>**  
 $(\text{CH}_3\text{CH}_2\text{O})_2\text{CHCH}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>7</sub>H<sub>15</sub>LiO<sub>2</sub>Si**  
 $(\text{CH}_3)_3\text{SiCH}(\text{Li})\text{CO}_2\text{C}_2\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>15</sub>LiS<sub>2</sub>Si**  
 $\overline{\text{S}(\text{CH}_2)_3\text{SC}(\text{Li})\text{Si}(\text{CH}_3)_3}$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>15</sub>NSi**  
 $(\text{C}_2\text{H}_5)_3\text{SiCN}$   
 Formation: 5.7.3.5
- C<sub>7</sub>H<sub>16</sub>GeOS**  
 $(\text{CH}_3)_3\text{Ge}\overline{\text{CHO}(\text{CH}_2)_3\text{S}}$   
 Reaction with RLi: 5.5.2.3.1
- C<sub>7</sub>H<sub>16</sub>LiNOSi**  
 $(\text{CH}_3)_3\text{SiCH}(\text{Li})\text{C}(\text{O})\text{N}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>16</sub>LiNSSI**  
 $(\text{CH}_3)_3\text{SiCH}(\text{Li})\text{C}(\text{S})\text{N}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>16</sub>LiN<sub>2</sub>OP**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CHP}(\text{O})(\text{NMe}_2)_2]^{-}\text{Li}^{+}$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>16</sub>LiN<sub>2</sub>O<sub>2</sub>P**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CHOP}(\text{O})(\text{NMe}_2)_2]^{-}\text{Li}^{+}$   
 Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>16</sub>OPbS**  
 $(\text{CH}_3)_3\text{Pb}\overline{\text{CHO}(\text{CH}_2)_3\text{S}}$   
 Transmetalation: 5.5.2.3.1
- C<sub>7</sub>H<sub>16</sub>OSSI**  
 $(\text{CH}_3)_3\text{Si}\overline{\text{CHO}(\text{CH}_2)_3\text{S}}$   
 Reaction with RLi: 5.5.2.3.1
- C<sub>7</sub>H<sub>16</sub>OSSn**  
 $(\text{CH}_3)_3\text{Sn}\overline{\text{CHO}(\text{CH}_2)_3\text{S}}$   
 Transmetalation: 5.5.2.3.1

- C<sub>7</sub>H<sub>16</sub>SeSi**  
1-(CH<sub>3</sub>)<sub>3</sub>Si-1-CH<sub>3</sub>SeC(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>16</sub>Sn**  
(CH<sub>3</sub>)CH=CHCH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>17</sub>GeLi**  
C<sub>2</sub>H<sub>5</sub>(i-C<sub>5</sub>H<sub>11</sub>)GeHLi  
Formation: 5.5.5.4
- C<sub>7</sub>H<sub>17</sub>LiOSi**  
(CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>OLi  
Formation: 5.5.4.2.1
- C<sub>7</sub>H<sub>18</sub>BrClSn<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Sn]<sub>2</sub>CClBr  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>18</sub>BrLiSi<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>CBrLi  
Formation: 5.5.2.3.3
- C<sub>7</sub>H<sub>18</sub>Br<sub>2</sub>Sn<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Sn]<sub>2</sub>CBr<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>18</sub>Cl<sub>2</sub>Sn<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Sn]<sub>2</sub>CCl<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>18</sub>Ge**  
C<sub>2</sub>H<sub>5</sub>(i-C<sub>5</sub>H<sub>11</sub>)GeH<sub>2</sub>  
Reaction with Li metal: 5.5.5.4, 5.5.5.4
- C<sub>7</sub>H<sub>18</sub>HgSn**  
i-C<sub>4</sub>H<sub>9</sub>HgSn(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.7.5.4
- C<sub>7</sub>H<sub>18</sub>LiP<sub>3</sub>**  
[(CH<sub>3</sub>)<sub>2</sub>P]<sub>3</sub>CLi  
Formation: 5.5.2.3.2
- C<sub>7</sub>H<sub>18</sub>Si<sub>2</sub>**  
(CH<sub>3</sub>)<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.7.3.3
- C<sub>7</sub>H<sub>19</sub>AuO**  
Au(CH<sub>3</sub>)<sub>3</sub>·OEt<sub>2</sub>  
Formation: 5.6.4.1
- C<sub>7</sub>H<sub>19</sub>BrHgSi<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>CHHgBr  
Formation: 5.7.2.3.2
- C<sub>7</sub>H<sub>19</sub>LiSi<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>CHLi  
Formation: 5.5.2.3.2  
Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
HC[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>Li  
Formation: 5.5.2.3.5
- C<sub>7</sub>H<sub>20</sub>OSiSn**  
(CH<sub>3</sub>)<sub>3</sub>SnCH<sub>2</sub>OSi(CH<sub>3</sub>)<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>7</sub>H<sub>20</sub>Si<sub>2</sub>**  
(CH<sub>3</sub>)<sub>2</sub>HSiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH(CH<sub>3</sub>)<sub>2</sub>  
Reaction with R<sub>2</sub>Hg: 5.7.3.3
- C<sub>7</sub>H<sub>20</sub>Sn<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Sn]<sub>2</sub>CH<sub>2</sub>  
Reaction with Na metal: 5.5.6.5
- C<sub>7</sub>H<sub>21</sub>HgNSi<sub>2</sub>**  
CH<sub>3</sub>HgN[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>  
Reaction with aliphatics: 5.7.2.3.4
- C<sub>8</sub>Cs**  
CsC<sub>8</sub>  
Formation: 5.5.3.1.2
- C<sub>8</sub>F<sub>4</sub>HgO<sub>4</sub>**  
[m-OC(O)C<sub>6</sub>F<sub>4</sub>C(O)O]Hg  
Decarboxylation: 5.7.2.3.7
- C<sub>8</sub>F<sub>8</sub>HgO<sub>2</sub>**  
C<sub>6</sub>F<sub>5</sub>HgOC(O)CF<sub>3</sub>  
Formation: 5.7.2.3.4
- C<sub>8</sub>F<sub>12</sub>HgN<sub>2</sub>**  
Hg[C(CN)(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>8</sub>F<sub>12</sub>Sn**  
(CF<sub>2</sub>=CF)<sub>4</sub>Sn  
Transmetallation: 5.5.2.3.1
- C<sub>8</sub>F<sub>14</sub>Hg**  
[CF<sub>3</sub>CF=CCF<sub>3</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.3
- C<sub>8</sub>F<sub>18</sub>Hg**  
[C(CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.3
- C<sub>8</sub>H<sub>2</sub>F<sub>16</sub>Hg**  
[H(CF<sub>2</sub>)<sub>4</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.2.1
- C<sub>8</sub>H<sub>3</sub>F<sub>5</sub>HgO<sub>2</sub>**  
CH<sub>3</sub>HgOC(O)C<sub>6</sub>F<sub>5</sub>  
Decarboxylation: 5.7.2.3.7  
C<sub>6</sub>F<sub>5</sub>HgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.7
- C<sub>8</sub>H<sub>3</sub>F<sub>6</sub>Li**  
2,4-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
2,6-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>4</sub>AgMnO<sub>3</sub>**  
[h<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub>]<sub>2</sub>Ag  
Reaction with CuI: 5.6.4.1
- C<sub>8</sub>H<sub>4</sub>BrHgMnO<sub>3</sub>**  
(CO)<sub>3</sub>MnC<sub>5</sub>H<sub>4</sub>HgBr  
Formation: 5.7.2.3.7
- C<sub>8</sub>H<sub>4</sub>BrHgO<sub>3</sub>Re**  
(CO)<sub>3</sub>ReC<sub>5</sub>H<sub>4</sub>HgBr-h<sup>5</sup>  
Formation: 5.7.2.3.1

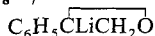
- $C_8H_4ClHgMnO_3$**   
 $(CO)_3MnC_5H_4HgCl-h^5$   
 Formation: 5.7.2.3.1, 5.7.2.3.7
- $C_8H_4ClHgO_3Re$**   
 $(CO)_3ReC_5H_4HgCl-h^5$   
 Formation: 5.7.2.3.7
- $C_8H_4CuMnO_3$**   
 $(CO)_3MnC_5H_4Cu-h^5$   
 Reaction with  $HgX_2$ : 5.7.2.3.1
- $C_8H_4LiO_3Re$**   
 $(CO)_3ReC_5H_4Li-h^5$   
 Reaction with  $HgX_2$ : 5.7.2.3.1
- $C_8H_5BrLiN$**   
 $p-BrC_6H_4CH(Li)CN$   
 Formation: 5.5.2.3.3
- $C_8H_5ClZn$**   
 $C_6H_5C\equiv CZnCl$   
 Formation: 5.7.2.4.1
- $C_8H_5F_3HgO_2$**   
 $C_6H_5HgOC(O)CF_3$   
 Formation: 5.7.2.3.4
- $C_8H_5K$**   
 $K[C_6H_5C\equiv C]$   
 Reaction with  $Cd(SCN)_2$ : 5.7.2.3.1
- $C_8H_5Li$**   
 $C_6H_5C\equiv CLi$   
 Formation: 5.5.2.3.2, 5.5.2.3.3
- $C_8H_5Na$**   
 $Na[C_6H_5C\equiv C]$   
 Formation: 5.5.3.3.1
- $C_8H_6BMnO_5$**   
 $(CO)_3MnC_5H_4B(OH)_2-h^5$   
 Reaction with  $HgX_2$ : 5.7.2.3.7
- $C_8H_6BO_5Re$**   
 $(CO)_3ReC_5H_4B(OH)_2-h^5$   
 Reaction with  $HgX_2$ : 5.7.2.3.7
- $C_8H_6ClHgNO_3$**   
 $2-NO_2-5-CH_3C(O)C_6H_3HgCl$   
 Formation: 5.7.2.3.7
- $C_8H_6ClLi$**   
 $(E)-C_6H_5CH=CClLi$   
 Formation: 5.5.2.3.2
- $C_8H_6Cl_2HgO_2$**   
 $2,5-Cl_2C_6H_3HgOC(O)CH_3$   
 Formation: 5.7.2.3.4  
 $(3,4-Cl_2C_6H_3)HgOC(O)CH_3$   
 Formation: 5.7.2.3.2
- $C_8H_6F_3LiSe$**   
 $m-CF_3C_6H_4SeCH_2Li$   
 Formation: 5.5.2.3.2
- $C_8H_6I_4Zn_2$**   
 $p-(CHIZnI)_2C_6H_4$   
 Formation: 5.7.2.3.5
- $C_8H_6LiN$**   
 $C_6H_5CH(CN)Li$   
 Formation: 5.5.2.3.2
- $C_8H_6LiNS$**   
 $C_6H_5SCH(Li)CN$   
 Formation: 5.5.2.3.2  
 $C_6H_5SCH(Li)NC$   
 Formation: 5.5.2.3.2
- $C_8H_6LiN_3$**   
 $NCHCLiNC_6H_5$   
 Formation: 5.5.2.3.2
- $C_8H_6Li_2O_2$**   
 $(C_6H_5)HC(Li)CO_2Li$   
 Formation: 5.5.2.3.5
- $C_8H_6Li_2O_2S$**   
 $C_6H_5SCH(Li)CO_2Li$   
 Formation: 5.5.2.3.2
- $C_8H_6Li_2O_2Se$**   
 $C_6H_5SeCH(Li)CO_2Li$   
 Formation: 5.5.2.3.2
- $C_8H_6Li_2O_3$**   
 $C_6H_5OCHLiCO_2Li$   
 Formation: 5.5.2.3.2
- $C_8H_7Ag$**   
 $AgCH=CHC_6H_5$   
 Formation: 5.6.4.1
- $C_8H_7BrHg$**   
 $trans-C_6H_5CH=CHHgBr$   
 Formation: 5.7.2.3.1
- $C_8H_7BrHgO_2$**   
 $n-CH_3O_2CC_6H_4HgBr$   
 Formation: 5.7.2.3.2  
 $p-BrC_6H_4HgOC(O)CH_3$   
 Formation: 5.7.2.3.6
- $C_8H_7ClHgO_2$**   
 $p-ClC_6H_4HgOC(O)CH_3$   
 Formation: 5.7.2.3.7
- $C_8H_7Cl_5Si$**   
 $C_6Cl_5(CH_3)_2HSi$   
 Transmetalation: 5.5.2.3.1
- $C_8H_7F_5Si$**   
 $C_6F_5(CH_3)_2SiH$   
 Reaction with  $[(R_3Si)_2N]_2Hg$ : 5.7.3.5  
 Transmetalation: 5.5.2.3.1
- $C_8H_7HgIO$**   
 $C_6H_5C(O)CH_2HgI$   
 Formation: 5.7.2.3.2
- $C_8H_7HgNO$**   
 $o-CH_3C_6H_4HgCNO$   
 Formation: 5.7.2.3.2
- $C_8H_7HgNO_4$**   
 $p-NO_2C_6H_4HgOC(O)CH_3$   
 Formation: 5.7.2.3.6

**C<sub>8</sub>H<sub>7</sub>Li**

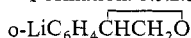
Formation: 5.5.2.3.3



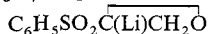
Formation: 5.5.2.3.1, 5.5.2.3.4

**C<sub>8</sub>H<sub>7</sub>LiO**

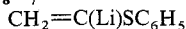
Formation: 5.5.2.3.2



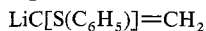
Formation: 5.5.2.3.3

**C<sub>8</sub>H<sub>7</sub>LiO<sub>3</sub>S**

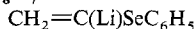
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>7</sub>LiS**

Formation: 5.5.2.3.2



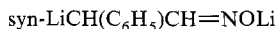
Formation: 5.5.2.3.1

**C<sub>8</sub>H<sub>7</sub>LiSe**

Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>7</sub>Li<sub>2</sub>NO**

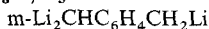
Formation: 5.5.2.3.2



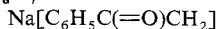
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>7</sub>Li<sub>2</sub>NS**

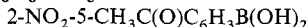
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>7</sub>Li<sub>3</sub>**

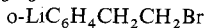
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>7</sub>NaO**

Formation: 5.5.3.3.1

**C<sub>8</sub>H<sub>8</sub>BNO<sub>5</sub>**Reaction with  $\text{HgX}_2$ : 5.7.2.3.7**C<sub>8</sub>H<sub>8</sub>BrHgLiO**

Reaction with Li metal: 5.5.2.2.2

**C<sub>8</sub>H<sub>8</sub>BrLi**

Formation: 5.5.2.3.3

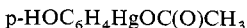
**C<sub>8</sub>H<sub>8</sub>HgO<sub>2</sub>**

Formation: 5.7.2.3.6

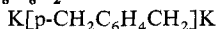
Reaction with arylhydrazines: 5.7.2.3.6

**C<sub>8</sub>H<sub>8</sub>HgO<sub>3</sub>**

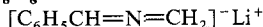
Formation: 5.7.2.3.4



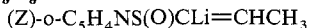
Formation: 5.7.2.3.4

**C<sub>8</sub>H<sub>8</sub>K<sub>2</sub>**

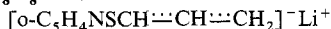
Formation: 5.5.3.3.1

**C<sub>8</sub>H<sub>8</sub>LiN**

Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>8</sub>LiNOS**

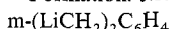
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>8</sub>LiNS**

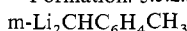
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>8</sub>Li<sub>2</sub>**

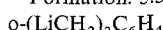
Formation: 5.5.2.2.3, 5.5.2.3.2



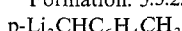
Formation: 5.5.2.3.2



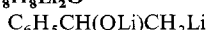
Formation: 5.5.2.3.2



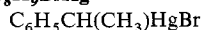
Formation: 5.5.2.3.2



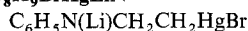
Formation: 5.5.2.3.2

**C<sub>8</sub>H<sub>8</sub>Li<sub>2</sub>O**

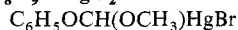
Formation: 5.5.2.2.2, 5.5.2.3.5

**C<sub>8</sub>H<sub>9</sub>BrHg**

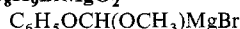
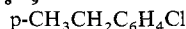
Formation: 5.7.2.3.1

**C<sub>8</sub>H<sub>9</sub>BrHgLiN**

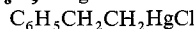
Reaction with Li metal: 5.5.2.2.2

**C<sub>8</sub>H<sub>9</sub>BrHgO<sub>2</sub>**

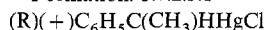
Formation: 5.7.2.3.1

**C<sub>8</sub>H<sub>9</sub>BrMgO<sub>2</sub>**Reaction with  $\text{HgX}_2$ : 5.7.2.3.1**C<sub>8</sub>H<sub>9</sub>Cl**

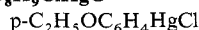
Reaction with Na metal: 5.5.3.2.1

**C<sub>8</sub>H<sub>9</sub>ClHg**

Formation: 5.7.2.3.1



Formation: 5.7.2.3.7

**C<sub>8</sub>H<sub>9</sub>ClHgO**

Formation: 5.7.2.3.6

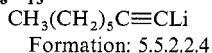
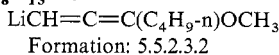
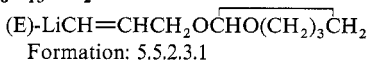
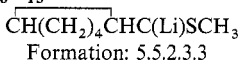
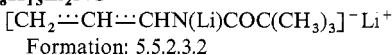
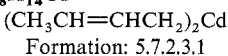
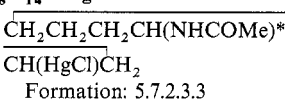
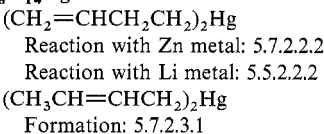
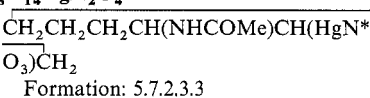
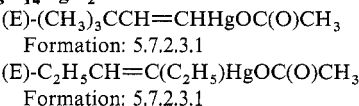
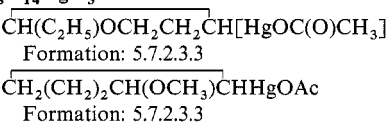
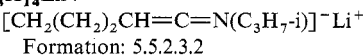
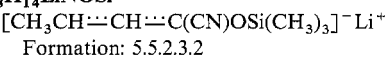
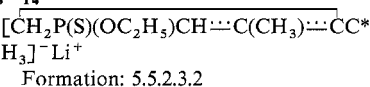
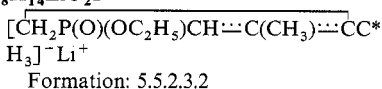
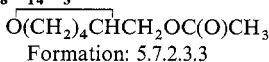
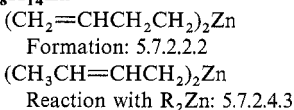
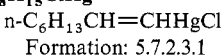
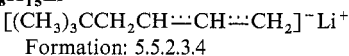
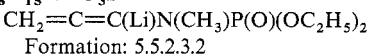
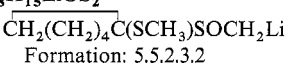
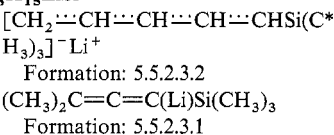
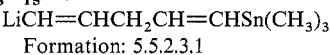
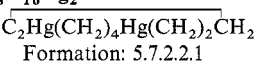
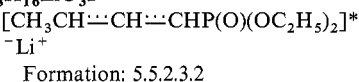
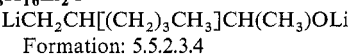
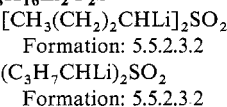
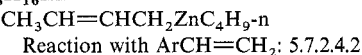
**C<sub>8</sub>H<sub>9</sub>ClHgO<sub>2</sub>**

Formation: 5.7.2.3.3

- C<sub>8</sub>H<sub>9</sub>Cs**  
Cs[C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>]  
Formation: 5.5.3.2.6
- C<sub>8</sub>H<sub>9</sub>Cu**  
Cu[C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>-2,6]  
Formation: 5.6.4.1
- C<sub>8</sub>H<sub>9</sub>HgI**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>HgCH<sub>2</sub>I  
Formation: 5.7.2.3.3
- C<sub>8</sub>H<sub>9</sub>Hg<sub>3</sub>NO<sub>3</sub>**  
[CH<sub>3</sub>C(O)Hg]<sub>3</sub>CCN  
Formation: 5.7.2.3.4
- C<sub>8</sub>H<sub>9</sub>Li**  
CH<sub>2</sub>CH<sub>2</sub>C(Li)C≡CCHCH<sub>2</sub>CH<sub>2</sub>  
Formation: 5.5.2.3.3  
C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)Li  
Formation: 5.5.2.2.5, 5.5.2.3.2  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.5  
m-CH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
o-CH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.2  
p-CH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
3,4-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.3
- C<sub>8</sub>H<sub>9</sub>LiO**  
C<sub>6</sub>H<sub>5</sub>CH(OCH<sub>3</sub>)Li  
Formation: 5.5.2.3.2  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>Li  
Formation: 5.5.2.3.1  
o-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.1  
p-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1  
2-CH<sub>3</sub>-4-CH<sub>3</sub>OC<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
2-Li-3-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2  
2-Li-5-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>LiOS**  
C<sub>6</sub>H<sub>5</sub>CH(Li)SOCH<sub>3</sub>  
Formation: 5.5.2.3.2  
C<sub>6</sub>H<sub>5</sub>SCH(OCH<sub>3</sub>)Li  
Formation: 5.5.2.3.2  
C<sub>6</sub>H<sub>5</sub>SOCH(Li)CH<sub>3</sub>  
Formation: 5.5.2.3.2  
m-LiCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2  
o-LiCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2
- p-LiCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2  
2-CH<sub>3</sub>O-3-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
2-CH<sub>3</sub>O-4-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
2-Li-3-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2  
2-Li-4-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2  
3-CH<sub>3</sub>O-2-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
3-Li-4-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>LiOSe**  
C<sub>6</sub>H<sub>5</sub>SeCH(OCH<sub>3</sub>)Li  
Formation: 5.5.2.3.1, 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>LiO<sub>2</sub>**  
2,3-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
2,4-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2  
2,6-(CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>LiO<sub>3</sub>S**  
C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>CH(OCH<sub>3</sub>)Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>LiS**  
C<sub>6</sub>H<sub>5</sub>SCH(CH<sub>3</sub>)Li  
Formation: 5.5.2.2.5  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>Li  
Formation: 5.5.2.3.1  
o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>Li  
Formation: 5.5.2.3.2  
o-CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.3.2  
3-CH<sub>3</sub>-2-CH<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>Li<sub>2</sub>N**  
CH<sub>3</sub>NLiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
C<sub>6</sub>H<sub>5</sub>N(Li)CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.2
- C<sub>8</sub>H<sub>9</sub>Li<sub>2</sub>NOS**  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N(Li)SOCH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>9</sub>Na**  
Na[C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>]  
Formation: 5.5.3.2.1  
Na[p-CH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]  
Formation: 5.5.3.2.1
- C<sub>8</sub>H<sub>10</sub>AgN**  
Ag[C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>-2]  
Formation; Complexes with CuX:  
5.6.4.1

- C<sub>8</sub>H<sub>10</sub>CdN<sub>4</sub>O<sub>4</sub>**  
[C<sub>2</sub>H<sub>5</sub>OC(O)C(N<sub>2</sub>)]<sub>2</sub>Cd  
Formation: 5.7.2.3.4
- C<sub>8</sub>H<sub>10</sub>Cl<sub>4</sub>Hg<sub>3</sub>O<sub>4</sub>**  
Hg[CCl(HgCl)OC(O)C<sub>2</sub>H<sub>5</sub>]<sub>2</sub>  
Formation: 5.7.2.3.3
- C<sub>8</sub>H<sub>10</sub>CuN**  
Cu[C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>]-2]  
Formation; Complexes with CuX:  
5.6.4.1
- C<sub>8</sub>H<sub>10</sub>Hg**  
bis(bicyclo[1.1.0]but-1-yl)mercury  
Formation: 5.7.2.3.1
- C<sub>6</sub>H<sub>5</sub>HgC<sub>2</sub>H<sub>5</sub>**  
Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>8</sub>H<sub>10</sub>HgN<sub>4</sub>O<sub>4</sub>**  
Hg[C(N<sub>2</sub>)CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>]<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>8</sub>H<sub>10</sub>HgO<sub>2</sub>S**  
C<sub>2</sub>H<sub>5</sub>Hg(O<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>)  
Formation: 5.7.2.3.2
- C<sub>8</sub>H<sub>10</sub>Li**  
Li[C<sub>8</sub>H<sub>10</sub>]<sup>-</sup>  
Reaction with Cd or CdCl<sub>2</sub>: 5.7.2.2.1
- C<sub>8</sub>H<sub>10</sub>LiN**  
o-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2
- p-[(CH<sub>3</sub>)<sub>2</sub>N]C<sub>6</sub>H<sub>4</sub>Li**  
Formation: 5.5.2.2.1
- C<sub>8</sub>H<sub>10</sub>LiNOS**  
C<sub>6</sub>H<sub>5</sub>S(O)(=NCH<sub>3</sub>)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>10</sub>LiNO<sub>2</sub>S**  
o-LiC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>10</sub>LiPS**  
(C<sub>6</sub>H<sub>5</sub>)P(S)(CH<sub>3</sub>)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>Zn**  
[C<sub>2</sub>H<sub>5</sub>OC(O)C(N<sub>2</sub>)]<sub>2</sub>Zn  
Formation: 5.7.2.3.4
- C<sub>8</sub>H<sub>11</sub>BO<sub>2</sub>**  
(R)(-)-C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)HB(OH)<sub>2</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.7
- C<sub>8</sub>H<sub>11</sub>ClGe**  
(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>GeCl  
Reaction with Li metal: 5.5.5.3
- C<sub>8</sub>H<sub>11</sub>ClSi**  
(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>SiCl  
Reaction with Li metal: 5.5.4.2.2, 5.5.4.3
- C<sub>8</sub>H<sub>11</sub>GeLi**  
(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>GeLi  
Formation: 5.5.5.3
- C<sub>8</sub>H<sub>11</sub>Li**  
Tricyclo[3.2.1.0<sup>2,4</sup>]oct-3-yllithium  
Formation: 5.5.2.3.3
- 3-Lithiotricyclo[3.2.1.0<sup>2,4</sup>]octane**  
Formation: 5.5.2.2.1
- C<sub>8</sub>H<sub>11</sub>LiO<sub>2</sub>**  
CH<sub>3</sub>OC=CHCH<sub>2</sub>CH=C(OCH<sub>3</sub>)CHLi  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>11</sub>LiO<sub>5</sub>**  
C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>CCLiCH(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)O  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>11</sub>LiSi**  
(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>SiLi  
Formation: 5.5.4.3, 5.5.4.2.1, 5.5.4.2.2
- C<sub>8</sub>H<sub>12</sub>**  
CH=CHCH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>  
Reaction with Hg(OAc)<sub>2</sub>: 5.7.2.3.3
- C<sub>8</sub>H<sub>12</sub>HgN<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>2</sub>CCN]<sub>2</sub>Hg  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.6
- C<sub>8</sub>H<sub>12</sub>HgO<sub>4</sub>**  
CH<sub>3</sub>C(O)OHgCHCH<sub>2</sub>CH[OC(O)CH<sub>3</sub>]<sup>-</sup>C\*  
H<sub>2</sub>  
Formation: 5.7.2.3.3
- C<sub>8</sub>H<sub>12</sub>Li<sub>2</sub>O<sub>2</sub>**  
[CH<sub>2</sub>···C(C<sub>4</sub>H<sub>9-n</sub>)···CHCO<sub>2</sub>Li]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2
- C<sub>8</sub>H<sub>12</sub>Pb**  
(CH<sub>2</sub>=CH)<sub>4</sub>Pb  
Reaction with group-IA metals: 5.5.7.3  
Reaction with Li metal: 5.5.2.2.2  
Transmetallation: 5.5.2.3.1
- C<sub>8</sub>H<sub>12</sub>Sn**  
(CH<sub>2</sub>=CH)<sub>4</sub>Sn  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
Reaction with Li metal: 5.5.2.2.2  
Transmetallation: 5.5.2.3.1
- C<sub>8</sub>H<sub>13</sub>ClHgO<sub>2</sub>**  
(CH<sub>3</sub>CO)<sub>2</sub>CHCH(CH<sub>3</sub>)CH<sub>2</sub>HgCl  
Formation: 5.7.2.3.3
- C<sub>8</sub>H<sub>13</sub>ClHgO<sub>3</sub>**  
CH<sub>3</sub>C(O)CH[C(O)OC<sub>2</sub>H<sub>5</sub>]CH<sub>2</sub>CH<sub>2</sub>HgCl  
Formation: 5.7.2.3.3
- C<sub>8</sub>H<sub>13</sub>Li**  
CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>C(Li)=CH  
Formation: 5.5.2.2.1
- [CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>C···CH···CH<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>**  
Formation: 5.5.2.3.1
- CH<sub>2</sub>=CHCH<sub>2</sub>CH(Li)CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>**  
Formation: 5.5.2.2.1
- CH<sub>3</sub>CH=CHCH<sub>2</sub>CH=CHCH<sub>2</sub>CH<sub>2</sub>Li**  
Formation: 5.5.2.2.1



**C<sub>8</sub>H<sub>13</sub>Li** *contd.***C<sub>8</sub>H<sub>13</sub>LiO****C<sub>8</sub>H<sub>13</sub>LiO<sub>2</sub>****C<sub>8</sub>H<sub>13</sub>LiS****C<sub>8</sub>H<sub>13</sub>Li<sub>2</sub>NO****C<sub>8</sub>H<sub>14</sub>Cd****C<sub>8</sub>H<sub>14</sub>ClHgNO****C<sub>8</sub>H<sub>14</sub>Hg****C<sub>8</sub>H<sub>14</sub>HgN<sub>2</sub>O<sub>4</sub>****C<sub>8</sub>H<sub>14</sub>HgO<sub>2</sub>****C<sub>8</sub>H<sub>14</sub>HgO<sub>3</sub>****C<sub>8</sub>H<sub>14</sub>LiN****C<sub>8</sub>H<sub>14</sub>LiNOSi****C<sub>8</sub>H<sub>14</sub>LiOPS****C<sub>8</sub>H<sub>14</sub>LiO<sub>2</sub>P****C<sub>8</sub>H<sub>14</sub>O<sub>3</sub>****C<sub>8</sub>H<sub>14</sub>Zn****C<sub>8</sub>H<sub>15</sub>ClHg****C<sub>8</sub>H<sub>15</sub>Li****C<sub>8</sub>H<sub>15</sub>LiNO<sub>3</sub>P****C<sub>8</sub>H<sub>15</sub>LiOS<sub>2</sub>****C<sub>8</sub>H<sub>15</sub>LiSi****C<sub>8</sub>H<sub>15</sub>LiSn****C<sub>8</sub>H<sub>16</sub>Hg<sub>2</sub>****C<sub>8</sub>H<sub>16</sub>LiO<sub>3</sub>P****C<sub>8</sub>H<sub>16</sub>Li<sub>2</sub>O****C<sub>8</sub>H<sub>16</sub>Li<sub>2</sub>O<sub>2</sub>S****C<sub>8</sub>H<sub>16</sub>Zn**

- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{ZnC}_4\text{H}_9\text{-t}$   
 Reaction with  $\text{ArCH}=\text{CH}_2$ : 5.7.2.4.2
- $\text{C}_8\text{H}_{16}\text{Zn}_2$**   
 $\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{ZnCH}_2(\text{CH}_2)_2\text{CH}_2$   
 Formation: 5.7.2.2.1
- $\text{C}_8\text{H}_{17}\text{BrMg}$**   
 $\text{C}_8\text{H}_{17}\text{MgBr}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- $\text{C}_8\text{H}_{17}\text{CHgSi}$**   
 $(\text{C}_2\text{H}_5)_3\text{SiCH}=\text{CHHgCl}$   
 Formation: 5.7.2.3.1
- $\text{C}_8\text{H}_{17}\text{K}$**   
 $\text{K}[\text{CH}_3(\text{CH}_2)_6\text{CH}_2]$   
 Formation: 5.5.3.3.2
- $\text{C}_8\text{H}_{17}\text{Li}$**   
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.2.1, 5.5.2.3.5  
 $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.2.1, 5.5.2.3.3, 5.5.2.3.5  
 Transmetallation: 5.5.2.3.1  
 $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1, 5.5.2.2.5, 5.5.2.3.5  
 Substrate in metal-metal exchange:  
 5.5.3.3.2
- $\text{C}_8\text{H}_{17}\text{LiO}$**   
 $\text{LiCH}(\text{OCH}_3)\text{C}_6\text{H}_{13}$   
 Formation: 5.5.2.3.1
- $\text{C}_8\text{H}_{18}\text{ClLiSi}$**   
 $(\text{CH}_3)_3\text{SiCCl}(\text{Li})\text{C}_4\text{H}_9\text{-n}$   
 Formation: 5.5.2.3.3
- $\text{C}_8\text{H}_{18}\text{Cl}_2\text{Ge}$**   
 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{GeCl}_2$   
 Reaction with K metal: 5.5.5.3
- $\text{C}_8\text{H}_{18}\text{GeK}_2$**   
 $\text{K}_2[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Ge}]$   
 Formation: 5.5.5.3
- $\text{C}_8\text{H}_{18}\text{Hg}$**   
 $(\text{n-C}_4\text{H}_9)_2\text{Hg}$   
 Formation: 5.7.2.3.1  
 Reaction with K or Cs metal: 5.5.3.2.3  
 Reaction with  $\text{PhX}_2\text{GeH}$ : 5.7.4.2  
 $(\text{s-C}_4\text{H}_9)_2\text{Hg}$   
 Formation: 5.7.2.3.2  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.2  
 Reaction with Zn metal: 5.7.2.2.2  
 Transmetallation: 5.5.2.3.1  
 $(\text{t-C}_4\text{H}_9)_2\text{Hg}$   
 Reaction with  $\text{R}_2\text{SnH}_2$ : 5.7.5.2.3  
 Reaction with  $\text{R}_3\text{SnH}$ : 5.7.5.2.3
- $\text{C}_8\text{H}_{18}\text{LiO}_5\text{P}$**   
 $(\text{C}_2\text{H}_5\text{O})_2\text{POCH}(\text{Li})\text{OCH}_2\text{CH}_2\text{OCH}_3$   
 Formation: 5.5.2.3.2
- $\text{C}_8\text{H}_{18}\text{LiP}$**   
 $\text{C}_5\text{H}_{11}\text{CH}_2\text{P}(\text{CH}_3)\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- $\text{C}_8\text{H}_{18}\text{Na}_2\text{Sn}$**   
 $\text{Na}_2[(\text{n-C}_4\text{H}_9)_2\text{Sn}]$   
 Formation: 5.5.6.2.2  
 $\text{Na}_2[(\text{s-C}_4\text{H}_9)_2\text{Sn}]$   
 Formation: 5.5.6.2.2
- $\text{C}_8\text{H}_{18}\text{Sn}$**   
 $(\text{n-C}_4\text{H}_9)_2\text{Sn}$   
 Formation: 5.5.6.2.1  
 Reaction with  $\text{RLi}$ : 5.5.6.2.1
- $\text{C}_8\text{H}_{18}\text{Zn}$**   
 $(\text{C}_4\text{H}_9)_2\text{Zn}$   
 Formation: 5.7.2.3.1  
 $(\text{n-C}_4\text{H}_9)_2\text{Zn}$   
 Formation: 5.7.2.2.1  
 $(\text{s-C}_4\text{H}_9)_2\text{Zn}$   
 Formation: 5.7.2.2.2  
 $(\text{t-C}_4\text{H}_9)_2\text{Zn}$   
 Reaction with  $\text{CH}_2=\text{CHR}$ : 5.7.2.4.2
- $\text{C}_8\text{H}_{19}\text{LiN}_2\text{OP}$**   
 $[\text{CH}_2\text{:CH:CHN}(\text{CH}_3)\text{P}(\text{O})\text{NMe}_2]^*\text{Li}^+$   
 Formation: 5.5.2.3.2
- $\text{C}_8\text{H}_{19}\text{LiSi}$**   
 $(\text{CH}_3)_3\text{SiCH}(\text{Li})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$   
 Formation: 5.5.2.2.5
- $\text{C}_8\text{H}_{20}\text{AlNa}$**   
 $\text{Na}[(\text{C}_2\text{H}_5)_4\text{Al}]$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.1
- $\text{C}_8\text{H}_{20}\text{BaZn}$**   
 $\text{Ba}[\text{Zn}(\text{C}_2\text{H}_5)_4]$   
 Formation and structure: 5.7.2.4.3
- $\text{C}_8\text{H}_{20}\text{CaZn}$**   
 $\text{Ca}[\text{Zn}(\text{C}_2\text{H}_5)_4]$   
 Formation and structure: 5.7.2.4.3
- $\text{C}_8\text{H}_{20}\text{Cu}_2\text{P}_2$**   
 $(\text{CH}_3)_2\text{P}(\text{CH}_2\text{CuCH}_2)_2\text{P}(\text{CH}_3)_2$   
 Formation: 5.6.4.3
- $\text{C}_8\text{H}_{20}\text{Ge}$**   
 $(\text{C}_2\text{H}_5)_4\text{Ge}$   
 Formation: 5.7.4.2  
 Reaction with K metal: 5.5.5.5
- $\text{C}_8\text{H}_{20}\text{GeHg}$**   
 $(\text{C}_2\text{H}_5)_3\text{GeHgC}_2\text{H}_5$   
 Formation: 5.7.4.2
- $\text{C}_8\text{H}_{20}\text{GeO}$**   
 $(\text{C}_2\text{H}_5)_3\text{GeOC}_2\text{H}_5$   
 Formation: 5.5.5.2.2
- $\text{C}_8\text{H}_{20}\text{HgSi}$**   
 $(\text{C}_2\text{H}_5)_3\text{SiHgC}_2\text{H}_5$   
 Formation: 5.7.3.3

**C<sub>8</sub>H<sub>20</sub>HgSi** *contd.*Reaction with R<sub>3</sub>GeH: 5.7.4.2Reaction with R<sub>3</sub>SiH: 5.7.3.3

Reaction with Li metal: 5.5.4.6

**C<sub>8</sub>H<sub>20</sub>HgSn**SnHgC<sub>2</sub>H<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

Formation: 5.7.5.4

**C<sub>8</sub>H<sub>20</sub>O<sub>4</sub>Sn**[CH<sub>3</sub>OCH<sub>2</sub>]<sub>4</sub>Sn

Transmetallation: 5.5.2.3.1

**C<sub>8</sub>H<sub>20</sub>Pb**(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb

Manufacture from Na-Pb: 5.5.7.1.2

Reaction with group-IA metals: 5.5.7.3

**C<sub>8</sub>H<sub>20</sub>Sn**(i-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>SnH<sub>2</sub>Reaction with R<sub>2</sub>Hg: 5.7.5.2.3(n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>SnH<sub>2</sub>Reaction with R<sub>2</sub>Hg: 5.7.5.2.3(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>SnH<sub>2</sub>Reaction with R<sub>2</sub>Hg: 5.7.5.2.3**C<sub>8</sub>H<sub>20</sub>SrZn**Sr[Zn(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]

Formation and structure: 5.7.2.4.3

**C<sub>8</sub>H<sub>22</sub>CdSi<sub>2</sub>**Cd[CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>

Formation: 5.7.2.3.1

**C<sub>8</sub>H<sub>22</sub>Ge<sub>2</sub>HgSi<sub>2</sub>**[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Ge]<sub>2</sub>Hg

Formation: 5.7.4.4

**C<sub>8</sub>H<sub>22</sub>HgSi<sub>2</sub>**[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>2</sub>HgReaction with X<sub>3</sub>GeH: 5.7.4.2Reaction with X<sub>3</sub>SiH: 5.7.3.3Reaction with SiX<sub>4</sub>: 5.7.3.3

Reaction with Zn metal: 5.7.2.2.2

**C<sub>8</sub>H<sub>22</sub>Si<sub>2</sub>Zn**[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>2</sub>Zn

Formation: 5.7.2.2.2, 5.7.2.3.1

**C<sub>8</sub>H<sub>26</sub>B<sub>10</sub>GeHg**(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>GeHg(C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)

Formation: 5.7.4.6

**C<sub>8</sub>H<sub>28</sub>Si<sub>5</sub>**[(CH<sub>3</sub>)<sub>2</sub>HSi]<sub>4</sub>Si

Reaction with RLi: 5.5.4.2.2

**C<sub>8</sub>K**KC<sub>8</sub>

Formation: 5.5.3.1.2

**C<sub>8</sub>Rb**RbC<sub>8</sub>

Formation: 5.5.3.1.2

**C<sub>9</sub>H<sub>4</sub>F<sub>6</sub>Li<sub>2</sub>O**o-LiC<sub>6</sub>H<sub>4</sub>C(CF<sub>3</sub>)<sub>2</sub>OLi

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>4</sub>Li<sub>4</sub>**o-LiC<sub>6</sub>H<sub>4</sub>C≡CCLi<sub>3</sub>

Formation: 5.5.2.3.2

p-LiC<sub>6</sub>H<sub>4</sub>C≡CCLi<sub>3</sub>

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>5</sub>ClCrHgO<sub>3</sub>**(CO)<sub>3</sub>CrC<sub>6</sub>H<sub>5</sub>HgCl-h<sup>6</sup>

Formation: 5.7.2.3.4, 5.7.2.3.7

**C<sub>9</sub>H<sub>5</sub>CrLiO<sub>3</sub>**(CO)<sub>3</sub>CrC<sub>6</sub>H<sub>5</sub>Li-h<sup>6</sup>

Formation: 5.5.2.3.1, 5.5.2.3.2

**C<sub>9</sub>H<sub>5</sub>F<sub>4</sub>Li**(E)-C<sub>6</sub>H<sub>5</sub>C(CF<sub>3</sub>)=CFLi

Formation: 5.5.2.3.3

**C<sub>9</sub>H<sub>5</sub>HgN**C<sub>6</sub>H<sub>5</sub>C≡CHgCN

Formation: 5.7.2.3.2

**C<sub>9</sub>H<sub>6</sub>CrO<sub>3</sub>**(CO)<sub>3</sub>CrC<sub>6</sub>H<sub>6</sub>-h<sup>6</sup>Reaction with HgX<sub>2</sub>: 5.7.2.3.4**C<sub>9</sub>H<sub>6</sub>F<sub>3</sub>LiSe**m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SeC(Li)=CH<sub>2</sub>

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>6</sub>LiN**(E)-C<sub>6</sub>H<sub>5</sub>CH=C(CN)Li

Formation: 5.5.2.3.2

(E)-C<sub>6</sub>H<sub>5</sub>CH=C(NC)Li

Formation: 5.5.2.3.2

(Z)-C<sub>6</sub>H<sub>5</sub>CH=C(CN)Li

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>6</sub>Li<sub>2</sub>**C<sub>6</sub>H<sub>5</sub>C≡CCHLi<sub>2</sub>

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>6</sub>Li<sub>2</sub>O<sub>2</sub>**(E)-C<sub>6</sub>H<sub>5</sub>CH=CLiCO<sub>2</sub>Li

Formation: 5.5.2.3.3

**C<sub>9</sub>H<sub>6</sub>Li<sub>2</sub>S**LiC≡CCH(Li)SC<sub>6</sub>H<sub>5</sub>

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>6</sub>Li<sub>2</sub>Se**LiC≡CCH(Li)SeC<sub>6</sub>H<sub>5</sub>

Formation: 5.5.2.3.2

**C<sub>9</sub>H<sub>7</sub>BCrO<sub>3</sub>**(CO)<sub>3</sub>CrC<sub>6</sub>H<sub>5</sub>B(OH)<sub>2</sub>-h<sup>6</sup>

Formation: 5.7.2.3.7

Reaction with HgX<sub>2</sub>: 5.7.2.3.7**C<sub>9</sub>H<sub>7</sub>ClHgO**cis-C<sub>6</sub>H<sub>5</sub>C(O)CH=CHHgCl

Formation: 5.7.2.3.2

**C<sub>9</sub>H<sub>7</sub>Li**C<sub>6</sub>H<sub>5</sub>C≡CCH<sub>2</sub>Li

Formation: 5.5.2.3.2

- Indenyllithium  
Formation: 5.5.2.2.4
- 1-Li-indene  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>7</sub>LiN<sub>2</sub>**  
 $\overline{\text{CHCHCHNC}_6\text{H}_4\text{Li-o}}$   
Formation: 5.5.2.3.2  
 $\overline{\text{CHCHC(Li)NC}_6\text{H}_5}$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>7</sub>Li<sub>2</sub>NO**  
 $\overline{\text{C(O)N(Li)CH(C}_6\text{H}_5\text{)CHLi}}$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>7</sub>Li<sub>2</sub>NO<sub>2</sub>S**  
 $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CLi}_2\text{NC}$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>8</sub>FLi**  
 $\overline{\text{C}_6\text{H}_5\text{CHCH}_2\text{CFLi}}$   
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>LiOSe**  
 $\text{m-CF}_3\text{C}_6\text{H}_4\text{SeCH(Li)OCH}_3$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>8</sub>Li<sub>2</sub>**  
 $[\text{C}_6\text{H}_5\text{CH}\cdots\text{CH}\cdots\text{CHLi}]^-\text{Li}^+$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>8</sub>Li<sub>2</sub>N<sub>2</sub>**  
 $\text{o-LiC}_6\text{H}_4\text{C}\equiv\text{NCH}_2\text{CH}_2\text{NLi}$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>8</sub>Li<sub>2</sub>O<sub>2</sub>**  
 $\text{p-LiC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{Li}$   
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>8</sub>Li<sub>2</sub>O<sub>3</sub>S**  
 $(\text{E})\text{-LiOCH}_2\text{CH}=\text{C(Li)SO}_2\text{C}_6\text{H}_5$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>BrMgO**  
 $\text{o-BrMgC}_6\text{H}_4\text{OCH}_2\text{CH}=\text{CH}_2$   
Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>9</sub>H<sub>9</sub>ClHgO**  
 $\text{p-CH}_3\text{C(O)C}_6\text{H}_4\text{HgCH}_2\text{Cl}$   
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>9</sub>ClHgO<sub>2</sub>**  
 $\text{p-C}_2\text{H}_5\text{OC(O)C}_6\text{H}_4\text{HgCl}$   
Formation: 5.7.2.3.6
- C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>LiS**  
 $2\text{-Li-5-CF}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_3$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>K**  
 $\text{K}[\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2]$   
Formation: 5.5.3.3.1
- C<sub>9</sub>H<sub>9</sub>Li**  
 $[\text{C}_6\text{H}_5\text{CH}\cdots\text{CH}\cdots\text{CH}_2]^-\text{Li}^+$   
Formation: 5.5.2.2.4, 5.5.2.3.1, 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>LiOS**  
 $[\text{CH}_2\cdots\text{CH}\cdots\text{CHSOC}_6\text{H}_5]^-\text{Li}^+$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>LiO<sub>2</sub>**  
 $\text{p-(OCH}_2\text{CHCH}_2\text{O)C}_6\text{H}_4\text{Li}$   
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>9</sub>LiO<sub>2</sub>S**  
 $\text{C}_6\text{H}_5\text{SCH(Li)CO}_2\text{CH}_3$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>LiO<sub>2</sub>Se**  
 $\text{C}_6\text{H}_5\text{SeCH(Li)CO}_2\text{CH}_3$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>LiO<sub>3</sub>**  
 $2\text{-CH}_3\text{O}_2\text{C-3-CH}_3\text{OC}_6\text{H}_3\text{Li}$   
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>9</sub>LiS**  
 $\overline{\text{C}_6\text{H}_5\text{SC(Li)CH}_2\text{CH}_2}$   
Formation: 5.5.2.2.5, 5.5.2.3.2  
 $\overline{\text{H}_2\text{CCH}_2\text{C(SC}_6\text{H}_5)\text{Li}}$   
Formation: 5.5.2.3.5
- C<sub>9</sub>H<sub>9</sub>LiSe**  
 $[\text{C}_6\text{H}_5\text{SeCH}\cdots\text{CH}\cdots\text{CH}_2]^-\text{Li}^+$   
Formation: 5.5.2.3.2  
 $1\text{-Li-1-C}_6\text{H}_5\text{Se}\overline{\text{CH}_2\text{CH}_2}$   
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>9</sub>Li<sub>2</sub>NO**  
 $\text{o-LiC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CONHLi}$   
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>9</sub>Li<sub>2</sub>NS**  
 $\text{CH}_3\text{CH(Li)C(S)N(C}_6\text{H}_5\text{)Li}$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>9</sub>Li<sub>3</sub>**  
 $1,3,5\text{-(LiCH}_2\text{)}_3\text{C}_6\text{H}_3$   
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>10</sub>**  
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$   
Reaction with  $\text{Hg(NO}_3\text{)}_2$ : 5.7.2.3.3
- C<sub>9</sub>H<sub>10</sub>HgO<sub>3</sub>**  
 $\text{o-CH}_3\text{OC}_6\text{H}_4\text{HgOC(O)CH}_3$   
Formation: 5.7.2.3.4  
 $\text{p-CH}_3\text{OC}_6\text{H}_4\text{HgOC(O)CH}_3$   
Formation: 5.7.2.3.4
- C<sub>9</sub>H<sub>10</sub>K**  
 $\text{K}[\overline{\text{CH(CH)}_7\text{CH}_2}]$   
Formation: 5.5.3.2.6
- C<sub>9</sub>H<sub>10</sub>K<sub>2</sub>**  
 $\text{K}_2[\overline{\text{CH(CH)}_7\text{CH}_2}]$   
Formation: 5.5.3.2.6
- C<sub>9</sub>H<sub>10</sub>Li**  
 $[\text{CH}\cdots(\text{CH})_7\cdots\text{CH}_2]^-\text{Li}^+$   
Formation: 5.5.2.3.2

- C<sub>9</sub>H<sub>10</sub>LiN**  
(Z)-LiCH=CHN(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>10</sub>LiNO<sub>3</sub>S**  
C<sub>6</sub>H<sub>5</sub>S(O)(=NCO<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>10</sub>LiNS<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>N=C(SCH<sub>3</sub>)SCH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>10</sub>Li<sub>2</sub>O**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)HC(OLi)CH<sub>2</sub>Li  
Formation: 5.5.2.3.5  
LiCH<sub>2</sub>CH(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>OLi  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>11</sub>BrHgLiN**  
C<sub>6</sub>H<sub>5</sub>N(Li)CH(CH<sub>3</sub>)CH<sub>2</sub>HgBr  
Reaction with Li metal: 5.5.2.2.2
- C<sub>9</sub>H<sub>11</sub>Cl**  
p-[(CH<sub>3</sub>)<sub>2</sub>CH]C<sub>6</sub>H<sub>4</sub>Cl  
Reaction with potassium metal: 5.5.3.2.1
- C<sub>9</sub>H<sub>11</sub>ClLiSi**  
(p-FC<sub>6</sub>H<sub>4</sub>)(CH<sub>3</sub>)<sub>2</sub>SiCHLiCl  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>11</sub>ClHgO<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>CH(OOH)CH<sub>2</sub>CH<sub>2</sub>HgCl  
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>11</sub>ClLiN**  
2-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>-3-ClC<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>11</sub>HgIO**  
p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>HgI  
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>11</sub>HgNO<sub>2</sub>**  
4-CH<sub>3</sub>C(O)OHg-2-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>9</sub>H<sub>11</sub>Hg<sub>2</sub>O<sub>4</sub>**  
(AcOHg)<sub>2</sub>C(CN)C(O)OC<sub>2</sub>H<sub>5</sub>  
Formation: 5.7.2.3.4
- C<sub>9</sub>H<sub>11</sub>K**  
K[C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>]  
Formation: 5.5.3.2.2  
Stability: 5.5.3.2.2  
Addition to C≡C: 5.5.3.3.3  
Formation: 5.5.3.2.1, 5.5.3.3.1  
K[p-(CH<sub>3</sub>)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>]  
Formation: 5.5.3.2.1
- C<sub>9</sub>H<sub>11</sub>Li**  
C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>Li  
Formation: 5.5.2.3.2, 5.5.2.3.5  
C<sub>6</sub>H<sub>5</sub>CH(Li)CH<sub>2</sub>CH<sub>3</sub>  
Formation: 5.5.2.3.4  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.5, 5.5.2.3.4
- m-(CH<sub>3</sub>)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
o-(CH<sub>3</sub>)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
p-(CH<sub>3</sub>)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li  
Formation: 5.5.2.2.1
- C<sub>9</sub>H<sub>11</sub>LiOSe**  
C<sub>6</sub>H<sub>5</sub>Se(O)C(CH<sub>3</sub>)<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>11</sub>LiO<sub>2</sub>**  
o-LiC<sub>6</sub>H<sub>4</sub>CH(OCH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2  
2-CH<sub>3</sub>OCH<sub>2</sub>O-4-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>11</sub>LiS**  
C<sub>2</sub>H<sub>5</sub>C(H)(SC<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.3.5  
C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.5
- C<sub>9</sub>H<sub>11</sub>Li<sub>2</sub>N**  
C<sub>6</sub>H<sub>5</sub>N(Li)CH(CH<sub>3</sub>)CH<sub>2</sub>Li  
Formation: 5.5.2.2.2
- C<sub>9</sub>H<sub>11</sub>N**  
C<sub>6</sub>H<sub>5</sub>NHCH<sub>2</sub>CH=CH<sub>2</sub>  
Reaction with Hg(OAc)<sub>2</sub>: 5.7.2.3.3
- C<sub>9</sub>H<sub>12</sub>AgN**  
Ag[(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)-2]  
Formation: 5.6.4
- C<sub>9</sub>H<sub>12</sub>Ag<sub>2</sub>BrN**  
Ag(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2) · AgBr  
Formation: 5.6.4.3
- C<sub>9</sub>H<sub>12</sub>ClHgN**  
o-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.2
- C<sub>9</sub>H<sub>12</sub>LiN**  
LiCH<sub>2</sub>N(CH<sub>3</sub>)CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1  
o-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.1  
2-(CH<sub>3</sub>)<sub>2</sub>N-5-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>12</sub>LiNO<sub>2</sub>**  
CHCHCHC(Li)N[C(O)OC(CH<sub>3</sub>)<sub>3</sub>]  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>12</sub>LiNO<sub>3</sub>S<sub>2</sub>**  
CH<sub>3</sub>S(O)(=NSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>13</sub>AuBr<sub>3</sub>N**  
AuBr<sub>3</sub>C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.6.4.3

- C<sub>9</sub>H<sub>13</sub>BO<sub>2</sub>**  
p-i-C<sub>3</sub>H<sub>7</sub>C<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.7
- C<sub>9</sub>H<sub>13</sub>ClHg**  
(CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.1
- C<sub>9</sub>H<sub>13</sub>Li**  
(CH<sub>3</sub>)<sub>3</sub>CC<sub>5</sub>H<sub>4</sub>Li  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>9</sub>H<sub>13</sub>LiO<sub>2</sub>Se**  
LiC(CH<sub>3</sub>)CHCHC[CH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>Se  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>13</sub>LiO<sub>3</sub>**  
LiCH(CCHOCHCH)OCH(CH<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>13</sub>LiS<sub>2</sub>**  
[S(CH<sub>2</sub>)<sub>3</sub>SC≡C≡CH(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>14</sub>LiNO**  
CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>C[CON(CH<sub>3</sub>)<sub>2</sub>]=CLi  
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>14</sub>LiNO<sub>2</sub>**  
(E)-CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NCLi=C(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)H  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>14</sub>Si**  
(CH<sub>3</sub>)<sub>3</sub>SiC<sub>6</sub>H<sub>5</sub>  
Formation: 5.7.3.1
- C<sub>9</sub>H<sub>15</sub>F<sub>3</sub>HgO<sub>3</sub>**  
CH<sub>3</sub>CH(OCH<sub>3</sub>)CHCH<sub>3</sub>CCH<sub>3</sub>[HgOC(O)\*  
CF<sub>3</sub>]<sub>2</sub>H  
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>15</sub>LiO**  
Li(C<sub>3</sub>H<sub>11</sub>)C=C=CHOCH<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>15</sub>LiOS<sub>2</sub>**  
OCH<sub>2</sub>CH(CH<sub>2</sub>)<sub>3</sub>CLiS(CH<sub>2</sub>)<sub>3</sub>S  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>15</sub>LiO<sub>3</sub>**  
LiC≡CC(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>15</sub>LiS<sub>2</sub>**  
C<sub>2</sub>H<sub>5</sub>C≡CC(Li)(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>16</sub>HgO<sub>2</sub>**  
CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH(HgOAc)CHCH<sub>3</sub>  
Reaction with alkenes: 5.7.2.3.3
- C<sub>9</sub>H<sub>16</sub>Li<sub>2</sub>O**  
LiCH<sub>2</sub>CH(cyclo-C<sub>6</sub>H<sub>11</sub>)CH<sub>2</sub>OLi  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>17</sub>ClHgO**  
(CH<sub>3</sub>)<sub>2</sub>COC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(HgCl)  
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>17</sub>Li**  
[C<sub>6</sub>H<sub>13</sub>CH≡CH≡CH<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>17</sub>LiO**  
LiCH<sub>2</sub>OCH(n-C<sub>4</sub>H<sub>9</sub>)C(CH<sub>3</sub>)=CH<sub>2</sub>  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>17</sub>LiOS**  
(E)-C<sub>2</sub>H<sub>5</sub>OCH=C(Li)SC<sub>5</sub>H<sub>11</sub>  
Formation: 5.5.2.3.1
- C<sub>9</sub>H<sub>17</sub>LiO<sub>2</sub>**  
S(O)CH<sub>2</sub>CH<sub>2</sub>CH[(CH<sub>3</sub>)<sub>3</sub>C]CH<sub>2</sub>CHLi  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>17</sub>LiO<sub>2</sub>**  
(CH<sub>3</sub>)<sub>2</sub>C=CLiCH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>17</sub>LiS<sub>2</sub>**  
H<sub>3</sub>C(CH<sub>2</sub>)<sub>4</sub>CLiS(CH<sub>2</sub>)<sub>3</sub>S  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>17</sub>LiS<sub>2</sub>**  
(H<sub>3</sub>C)<sub>3</sub>CCH<sub>2</sub>CLiS(CH<sub>2</sub>)<sub>3</sub>S  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>18</sub>ClLiO<sub>2</sub>Si**  
(CH<sub>3</sub>)<sub>3</sub>SiC(Li)ClCO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>18</sub>HgO<sub>3</sub>**  
(CH<sub>3</sub>)<sub>3</sub>CCH(OCH<sub>3</sub>)CH<sub>2</sub>HgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>18</sub>Li<sub>2</sub>O**  
LiCH<sub>2</sub>CH(n-C<sub>4</sub>H<sub>9</sub>)C(CH<sub>3</sub>)<sub>2</sub>OLi  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>19</sub>HgNO<sub>4</sub>**  
n-C<sub>6</sub>H<sub>13</sub>CH(OCH<sub>3</sub>)CH<sub>2</sub>HgNO<sub>3</sub>  
Formation: 5.7.2.3.3
- C<sub>9</sub>H<sub>19</sub>Li**  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.1
- C<sub>9</sub>H<sub>19</sub>LiNO<sub>3</sub>P**  
CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NCH(Li)P(O)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>19</sub>LiN<sub>2</sub>O**  
C<sub>8</sub>H<sub>17</sub>N=N(O)CH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>19</sub>LiO**  
(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH(Li)(CH<sub>2</sub>)<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>19</sub>LiOSi**  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH=C(Li)OSi(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.2.5
- C<sub>9</sub>H<sub>19</sub>LiO<sub>2</sub>Si**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(Li)CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>19</sub>LiO<sub>4</sub>Si<sub>2</sub>**  
LiCH[CO<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>  
Formation: 5.5.2.3.2

- C<sub>9</sub>H<sub>19</sub>LiSi**  
n-C<sub>4</sub>H<sub>9</sub>CH=C[Si(CH<sub>3</sub>)<sub>3</sub>]Li  
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>20</sub>ClLiO<sub>6</sub>P<sub>2</sub>**  
LiCCl[P(O)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>  
Formation: 5.5.2.3.3
- C<sub>9</sub>H<sub>20</sub>LiP**  
[(CH<sub>3</sub>)<sub>3</sub>C]<sub>2</sub>PCH<sub>2</sub>Li  
Formation: 5.5.2.3.2
- C<sub>9</sub>H<sub>20</sub>Sn**  
(CH<sub>3</sub>)<sub>3</sub>SnCH<sub>2</sub>C(CH<sub>3</sub>)=CHC<sub>2</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>9</sub>H<sub>21</sub>GeLi**  
(i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>GeLi  
Formation: 5.5.5.6
- C<sub>9</sub>H<sub>21</sub>LiSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(Li)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>9</sub>H<sub>21</sub>LiSn**  
(n-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>SnLi  
Formation: 5.5.6.3.1
- C<sub>9</sub>H<sub>21</sub>NaSn**  
Na[(i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6.2.2
- C<sub>9</sub>H<sub>22</sub>HgSn**  
C<sub>3</sub>H<sub>7</sub>HgSn(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Formation: 5.7.5.4
- C<sub>9</sub>H<sub>22</sub>Sn**  
(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3
- C<sub>9</sub>H<sub>27</sub>LiSi<sub>4</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>3</sub>SiLi  
Formation: 5.5.4.2.1, 5.5.4.2.2
- C<sub>9</sub>H<sub>27</sub>LiSn<sub>4</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Sn]<sub>3</sub>SnLi  
Formation: 5.5.6
- C<sub>10</sub>Cl<sub>10</sub>Hg**  
(h<sup>1</sup>-C<sub>5</sub>Cl<sub>5</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.4
- C<sub>10</sub>F<sub>8</sub>HgN<sub>2</sub>**  
(2-C<sub>5</sub>F<sub>4</sub>N)<sub>2</sub>Hg  
Formation: 5.7.2.3.7
- C<sub>10</sub>F<sub>18</sub>Hg**  
(C<sub>3</sub>F<sub>7</sub>CF=CF)<sub>2</sub>Hg  
Formation: 5.7.2.3.7
- C<sub>10</sub>F<sub>18</sub>HgO<sub>4</sub>**  
[CF<sub>3</sub>C(O)OC(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.3
- C<sub>10</sub>H<sub>6</sub>BrLi**  
1-Li-7-Br-Napthalene  
Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>6</sub>F<sub>4</sub>Hg<sub>2</sub>O<sub>2</sub>**  
1,2-[CH<sub>3</sub>C(O)Hg]<sub>2</sub>C<sub>6</sub>F<sub>4</sub>  
Formation: 5.7.2.3.7
- C<sub>10</sub>H<sub>6</sub>Hg**  
(CH<sub>3</sub>C≡CC≡C)<sub>2</sub>Hg  
Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>6</sub>Li<sub>2</sub>**  
2,7-Li<sub>2</sub>-Napthalene  
Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>7</sub>BrHg**  
1-C<sub>10</sub>H<sub>7</sub>HgBr  
Formation: 5.7.2.3.6
- C<sub>10</sub>H<sub>7</sub>ClZn**  
1-naphthylZnCl  
Formation: 5.7.2.3.2
- C<sub>10</sub>H<sub>7</sub>Li**  
1-Naphthyllithium  
Formation: 5.5.2.2.1, 5.5.2.3.3  
2-Naphthyllithium  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>7</sub>Li<sub>2</sub>N**  
o-LiC<sub>6</sub>H<sub>4</sub> $\overline{\text{CLi=CHCH=CH}}$   
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>8</sub>AgClFe**  
h<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>ClFeC<sub>5</sub>H<sub>4</sub>Ag-h<sup>5</sup>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>ClAg-h<sup>5</sup>  
Formation: 5.6.4.1
- C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>FeHg**  
h<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>ClFeC<sub>5</sub>H<sub>4</sub>HgCl-h<sup>5</sup>  
Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>FeHg<sub>2</sub>**  
(h<sup>5</sup>-ClHgC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe  
Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>LiSe**  
[m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SeCH≡CH≡CH<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>8</sub>FeK<sub>2</sub>**  
(h<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>K)<sub>2</sub>Fe  
Formation: 5.5.3.3.1
- C<sub>10</sub>H<sub>8</sub>FeNa<sub>2</sub>**  
(h<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Na)<sub>2</sub>Fe  
Formation: 5.5.3.3.1
- C<sub>10</sub>H<sub>8</sub>K**  
[C<sub>10</sub>H<sub>8</sub>]<sup>-</sup>K<sup>+</sup>  
Formation: 5.5.3.2.4
- C<sub>10</sub>H<sub>8</sub>K<sub>2</sub>**  
[C<sub>10</sub>H<sub>8</sub>]<sup>2-</sup>K<sup>+</sup>  
Formation: 5.5.3.2.4
- C<sub>10</sub>H<sub>8</sub>Li**  
[C<sub>10</sub>H<sub>8</sub>]<sup>-</sup>Li<sup>+</sup>  
Lithiating agent: 5.5.2.3.5  
Li naphthalide radical anion  
Reaction with RX: 5.5.2.2.1
- C<sub>10</sub>H<sub>8</sub>LiN<sub>2</sub>**  
Li 4,4'-bipyridine radical anion  
Formation: 5.5.2.2.3

- C<sub>10</sub>H<sub>8</sub>Li<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}(\text{CH}_3)\text{Li}_2$   
 Formation: 5.5.2.3.2  
 $[\text{C}_{10}\text{H}_8]^- 2\text{Li}^+$   
 Formation: 5.5.2.2.3, 5.5.3.2.4  
 dilithioazulene  
 Formation: 5.5.2.2.3
- C<sub>10</sub>H<sub>8</sub>Li<sub>2</sub>O**  
 $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}(\text{Li})_2\text{OCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>8</sub>Na**  
 $[\text{C}_{10}\text{H}_8]^- \text{Na}^+$   
 Base for metallation reaction: 5.5.3.3.1  
 Formation: 5.5.3.2.4
- C<sub>10</sub>H<sub>9</sub>ClFeHg**  
 $(\text{h}^5\text{-ClHgC}_5\text{H}_4)\text{FeC}_5\text{H}_5\text{-h}^5$   
 Formation: 5.7.2.3.4, 5.7.2.3.7  
 Transmetallation: 5.5.2.3.1
- C<sub>10</sub>H<sub>9</sub>F<sub>9</sub>Sn**  
 $\text{n-C}_4\text{H}_9\text{Sn}(\text{CF}=\text{CF}_2)_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>10</sub>H<sub>9</sub>FeLi**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{Li-h}^5$   
 Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>10</sub>H<sub>9</sub>Li**  
 $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}(\text{CH}_3)\text{HLi}$   
 Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>10</sub>BClFeO<sub>2</sub>**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Fe}[\text{C}_5\text{H}_5\text{ClB}(\text{OH})_2\text{-h}^5]$   
 Reaction with  $\text{Ag}^+$  cation: 5.6.4.1
- C<sub>10</sub>H<sub>10</sub>Cd**  
 $(\text{C}_5\text{H}_5)_2\text{Cd}$   
 Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>10</sub>Fe**  
 $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Fe}$   
 Metallation: 5.5.3.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.4
- C<sub>10</sub>H<sub>10</sub>Hg**  
 $(\text{C}_5\text{H}_5)_2\text{Hg}$   
 Reaction with  $\text{Hg}[\text{N}(\text{SiR}_3)_2]_2$ : 5.7.2.3.2  
 $(\text{h}^1\text{-C}_5\text{H}_5)_2\text{Hg}$   
 Formation: 5.7.2.3.1, 5.7.2.3.4
- C<sub>10</sub>H<sub>10</sub>HgN<sub>2</sub>**  
 $(\text{m-C}_5\text{H}_5\text{N})_2\text{Hg}$   
 Formation: 5.7.2.3.6
- C<sub>10</sub>H<sub>10</sub>Hg<sub>2</sub>O<sub>4</sub>**  
 $\text{m-}[\text{CH}_3\text{C}(\text{O})\text{OHg}]_2\text{C}_6\text{H}_4$   
 Formation: 5.7.2.3.7
- C<sub>10</sub>H<sub>10</sub>LiN**  
 $\text{o-LiC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{CN}$   
 Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>10</sub>Li<sub>2</sub>**  
 $[\text{C}_6\text{H}_5\text{CH}\equiv\text{C}(\equiv\text{CH}_2)_2]^{2-} 2\text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>10</sub>V**  
 $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{V}$   
 Reaction with  $(\text{R}_3\text{Ge})_2\text{Cd}$ : 5.7.4
- C<sub>10</sub>H<sub>10</sub>Zn**  
 $(\text{C}_5\text{H}_5)_2\text{Zn}$   
 Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>11</sub>BFeO<sub>2</sub>**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{B}(\text{OH})_2\text{-h}^5$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.7
- C<sub>10</sub>H<sub>11</sub>BrHg<sub>2</sub>O<sub>2</sub>S**  
 $\text{CH}_2(\text{BrHg})\text{CHS}(\text{O})(\text{O})\text{CH}(\text{HgBr})\text{CH}_2\text{N-}$   
 $\text{C}_6\text{H}_5$   
 Formation: 5.7.2.3.3
- C<sub>10</sub>H<sub>11</sub>HgNO<sub>3</sub>**  
 $\text{p-CH}_3\text{C}(\text{O})\text{OHgC}_6\text{H}_4\text{NHC}(\text{O})\text{CH}_3$   
 Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>11</sub>Hg<sub>2</sub>NO<sub>4</sub>**  
 $2,4\text{-}[\text{CH}_3\text{C}(\text{O})\text{OHg}]_2\text{C}_6\text{H}_3\text{NH}_2$   
 Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>11</sub>Li**  
 $\text{CH}(\text{CH}_3)\text{CH}(\text{Li})\text{CHC}_6\text{H}_5$   
 Formation: 5.5.2.3.4  
 $[\text{C}_6\text{H}_5\text{CH}\equiv\text{C}(\text{CH}_3)\equiv\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2  
 $(\text{E})\text{-C}_6\text{H}_5(\text{Li})\text{C}=\text{CHC}_2\text{H}_5$   
 Formation: 5.5.2.3.3  
 $(\text{Z})\text{-C}_6\text{H}_5(\text{Li})\text{C}=\text{CHC}_2\text{H}_5$   
 Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>11</sub>LiOS**  
 $[\text{C}_6\text{H}_5\text{SCH}\equiv\text{CH}\equiv\text{CHOCH}_3]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>11</sub>LiO<sub>2</sub>S**  
 $\text{C}_6\text{H}_5\text{SOCLi}=\text{CHCH}_2\text{OCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>11</sub>LiS**  
 $\text{CH}_3(\text{H})\text{CCH}_2\text{C}(\text{SC}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.2.3.5  
 $(\text{CH}_3)_2\text{C}=\text{C}(\text{SC}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.2.2.5, 5.5.2.3.5  
 $\text{C}_6\text{H}_5\text{SC}(\text{Li})\text{CH}(\text{CH}_3)\text{CH}_2$   
 Formation: 5.5.2.2.5
- C<sub>10</sub>H<sub>11</sub>LiSe**  
 $[\text{C}_6\text{H}_5\text{SeCH}\equiv\text{C}(\text{CH}_3)\equiv\text{CH}_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2  
 $(\text{C}_6\text{H}_5\text{Se})\text{LiC}(\text{CH}_2)_2\text{CH}_2$   
 Formation: 5.5.2.3.1
- C<sub>10</sub>H<sub>12</sub>BrLiO<sub>2</sub>**  
 $2\text{-BrCH}_2\text{CH}_2\text{-4,5-(CH}_3\text{O)}_2\text{C}_6\text{H}_2\text{Li}$   
 Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>12</sub>ClLi<sub>2</sub>NO**  
 $2\text{-}[(\text{CH}_3)_2\text{N}(\text{CH}_3)(\text{LiO})\text{C}]\text{-5-ClC}_6\text{H}_3\text{Li}$   
 Formation: 5.5.2.3.2



- C<sub>10</sub>H<sub>12</sub>HgO<sub>2</sub>**  
2,4-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>HgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>12</sub>LiN**  
(E)-(CH<sub>3</sub>)<sub>2</sub>N(C<sub>6</sub>H<sub>5</sub>)C=CHLi  
Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>12</sub>Li<sub>2</sub>**  
p-(LiCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>  
Formation: 5.5.2.2.5, 5.5.2.3.5
- C<sub>10</sub>H<sub>12</sub>Li<sub>2</sub>O**  
LiCH<sub>2</sub>CH(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>OLi  
Formation: 5.5.2.3.4
- C<sub>10</sub>H<sub>12</sub>Li<sub>2</sub>O<sub>4</sub>**  
LiC(CO<sub>2</sub>CH<sub>3</sub>)C(CO<sub>2</sub>CH<sub>3</sub>)(Li)CH<sub>2</sub>CH=\*  
CHCH<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>12</sub>OS**  
CH<sub>3</sub>OC(SC<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>CH<sub>2</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>10</sub>H<sub>12</sub>OZn**  
CH<sub>3</sub>CH=CHCH<sub>2</sub>ZnOC<sub>6</sub>H<sub>5</sub>  
Reaction with ArCH=CH<sub>2</sub>: 5.7.2.4.2
- C<sub>10</sub>H<sub>12</sub>Zn**  
CH<sub>3</sub>CH=CHCH<sub>2</sub>ZnC<sub>6</sub>H<sub>5</sub>  
Reaction with ArCH=CH<sub>2</sub>: 5.7.2.4.2
- C<sub>10</sub>H<sub>13</sub>K**  
K[CH(CH)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]  
Formation: 5.5.3.2.6
- C<sub>10</sub>H<sub>13</sub>Li**  
CH<sub>2</sub>CH<sub>2</sub>C=C(CHCH<sub>2</sub>CH<sub>2</sub>)C(Li)CH<sub>2</sub>C\*  
H<sub>2</sub>  
Formation: 5.5.2.3.3
- C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.3.5
- m-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.2
- p-CH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.5
- p-LiC<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- 2,6-(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>13</sub>LiO**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.5
- C<sub>6</sub>H<sub>5</sub>O(CH<sub>2</sub>)<sub>4</sub>Li  
Formation: 5.5.2.3.5
- o-LiC<sub>6</sub>H<sub>4</sub>OC(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>13</sub>LiS**  
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH(SC<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.2.5
- (CH<sub>3</sub>)<sub>2</sub>CHCH(SC<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.2.5, 5.5.2.3.2
- C<sub>6</sub>H<sub>5</sub>SCH(Li)CH(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>6</sub>H<sub>5</sub>SCH(Li)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>6</sub>H<sub>5</sub>S(CH<sub>2</sub>)<sub>4</sub>Li  
Formation: 5.5.2.3.5
- C<sub>10</sub>H<sub>13</sub>Li<sub>2</sub>NO**  
o-LiC<sub>6</sub>H<sub>4</sub>CHOLiCH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- o-LiC<sub>6</sub>H<sub>4</sub>C(OLi)(CH<sub>3</sub>)N(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>14</sub>AsLi**  
o-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AsC<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>14</sub>CuO<sub>2</sub>**  
[CH<sub>3</sub>C(O)CHC(O)CH<sub>3</sub>]<sub>2</sub>Cu(II)  
Reaction with organoaluminums:  
5.6.4.1
- C<sub>10</sub>H<sub>14</sub>HgO<sub>4</sub>**  
[CH<sub>3</sub>C(O)CHC(O)CH<sub>3</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>14</sub>HgO<sub>8</sub>**  
[(CH<sub>3</sub>O<sub>2</sub>C)<sub>2</sub>CH]<sub>2</sub>Hg  
Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>14</sub>LiN**  
o-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>14</sub>LiNO**  
2-Li-4-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2
- 3-Li-4-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>14</sub>O**  
C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>OCH<sub>3</sub>  
Reaction with Na-K or Cs metal:  
5.5.3.2.2
- C<sub>10</sub>H<sub>14</sub>OS**  
(CH<sub>3</sub>)<sub>2</sub>C(OCH<sub>3</sub>)SC<sub>6</sub>H<sub>5</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>10</sub>H<sub>14</sub>S**  
CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)SC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- (CH<sub>3</sub>)<sub>3</sub>CSC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>10</sub>H<sub>14</sub>Zn**  
(CH<sub>2</sub>=CHCH=CHCH<sub>2</sub>)<sub>2</sub>Zn  
Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>15</sub>Li**  
1-Lithioadamantane  
Formation: 5.5.2.2.1

- 1-Lithiotwistane  
Formation: 5.5.2.2.1
- 2-Lithioadamantane  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>14</sub>LiOSSi**  
C<sub>6</sub>H<sub>5</sub>SOCH(Li)Si(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>15</sub>LiO<sub>4</sub>**  
C(OCH<sub>3</sub>)<sub>2</sub>CH=CHC(OCH<sub>3</sub>)<sub>2</sub>CH=CLi  
Formation: 5.5.2.3.3
- C<sub>10</sub>H<sub>15</sub>LiSSi**  
C<sub>6</sub>H<sub>5</sub>SCH(Li)Si(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>15</sub>LiSeSi**  
C<sub>6</sub>H<sub>5</sub>SeCH(Li)Si(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>15</sub>LiSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(C<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.2.5  
C<sub>6</sub>H<sub>5</sub>CH(Li)Si(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.2.2  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.2  
C<sub>6</sub>H<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SiLi  
Formation: 5.5.4.2.1
- C<sub>10</sub>H<sub>15</sub>NaPb**  
Na[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>Pb]  
Formation: 5.5.7.3
- C<sub>10</sub>H<sub>16</sub>SSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>10</sub>H<sub>17</sub>Li**  
CH<sub>3</sub>C(CH<sub>2</sub>)<sub>3</sub>CH(CH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CHLi  
Formation: 5.5.2.3.4  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>C≡CLi  
Formation: 5.5.2.2.4  
(CH<sub>3</sub>)<sub>3</sub>CCHCH<sub>2</sub>CH=C(Li)CH<sub>2</sub>CH<sub>2</sub>  
Reaction with RX: 5.5.2.2.1  
Li phenanthrene radical anion  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>16</sub>B<sub>3</sub>LiO<sub>6</sub>**  
LiC[BO(CH<sub>2</sub>)<sub>2</sub>O]<sub>3</sub>  
Formation: 5.5.2.3.1
- C<sub>10</sub>H<sub>18</sub>Hg**  
[C<sub>2</sub>H<sub>5</sub>(CH<sub>3</sub>)C=CH]<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>18</sub>HgO<sub>2</sub>**  
n-C<sub>6</sub>H<sub>13</sub>CH=CHHgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>18</sub>LiN**  
[(CH<sub>3</sub>)<sub>2</sub>C=CH=NC<sub>6</sub>H<sub>11</sub>-cyclo]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2
- C<sub>5</sub>H<sub>11</sub>C≡CCH(Li)N(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>18</sub>Sn**  
n-C<sub>4</sub>H<sub>9</sub>(CH<sub>2</sub>=CH)<sub>3</sub>Sn  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>10</sub>H<sub>18</sub>Zn**  
CH<sub>3</sub>CH=CHCH<sub>2</sub>ZnC<sub>6</sub>H<sub>11</sub>  
Reaction with ArCH=CH<sub>2</sub>: 5.7.2.4.2
- C<sub>10</sub>H<sub>19</sub>KO**  
K[CH<sub>2</sub>CH(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH\*  
O]  
Metal exchange with RLi: 5.5.3.3.1  
Reagent for metal-metal exchange:  
5.5.3.3.2
- C<sub>10</sub>H<sub>19</sub>Li**  
(CH<sub>3</sub>)<sub>3</sub>CCHCH<sub>2</sub>CH<sub>2</sub>CH(Li)CH<sub>2</sub>CH<sub>2</sub>  
Formation: 5.5.2.2.1  
Me<sub>2</sub>CHCHCH(Li)CH<sub>2</sub>CH(Me)CH<sub>2</sub>CH<sub>2</sub>  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>20</sub>CdF<sub>4</sub>O<sub>2</sub>P<sub>2</sub>**  
[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>P(O)CF<sub>2</sub>]<sub>2</sub>Cd  
Formation: 5.7.2.2.1
- C<sub>10</sub>H<sub>20</sub>ClHg**  
trans-4-(CH<sub>3</sub>)<sub>3</sub>C-cyclo-C<sub>6</sub>H<sub>11</sub>HgCl  
Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>20</sub>LiO<sub>5</sub>P**  
(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)CH(Li)OCHO(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>10</sub>H<sub>20</sub>Li<sub>2</sub>**  
LiCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>21</sub>GeHgN**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>GeHgC(CH<sub>3</sub>)<sub>2</sub>CN  
Formation: 5.7.4.6
- C<sub>10</sub>H<sub>21</sub>HgN<sub>2</sub>O<sub>7</sub>**  
(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NC(O)[(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)]CHHgN\*  
O<sub>3</sub>  
Formation: 5.7.2.3.4
- C<sub>10</sub>H<sub>21</sub>Li**  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.1
- C<sub>10</sub>H<sub>21</sub>LiO**  
(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH(Li)C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>10</sub>H<sub>21</sub>LiO<sub>2</sub>**  
LiCH(C<sub>5</sub>H<sub>11</sub>)OCH(CH<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1
- C<sub>10</sub>H<sub>22</sub>BLiO<sub>2</sub>Si**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(Li)BOC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O  
Formation: 5.5.2.3.2

- C<sub>10</sub>H<sub>22</sub>Cd**  
 $[(CH_3)_2CH(CH_2)_2]_2Cd$   
 Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>22</sub>Hg**  
 $[CH_3CH_2CH(CH_3)CH_2]_2Hg$   
 Reaction with Li metal: 5.5.2.2.2  
 $[CH_3(CH_2)_4]_2Hg$   
 Formation: 5.7.2.2.1  
 Reaction with Na or K metal: 5.5.3.2.3
- C<sub>10</sub>H<sub>22</sub>HgSi<sub>2</sub>**  
 $[(E)-(CH_3)_3SiCH=CH]_2Hg$   
 Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>22</sub>O<sub>2</sub>Zn**  
 $[CH_3O(CH_2)_4]_2Zn$   
 Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>22</sub>S<sub>2</sub>Zn**  
 $[C_2H_5S(CH_2)_3]_2Zn$   
 Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>22</sub>Zn**  
 $(cyclo-C_5H_{11})_2Zn$   
 Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>24</sub>As<sub>2</sub>Hg**  
 $[(CH_3)_2As(CH_2)_3]_2Hg$   
 Formation: 5.7.2.3.1
- C<sub>10</sub>H<sub>24</sub>CuOP**  
 $t-C_4H_9OCu \cdot PEt_3$   
 Reaction with RH: 5.6.4.3
- C<sub>10</sub>H<sub>24</sub>HgSn**  
 $i-C_4H_9HgSn(C_2H_5)_3$   
 Formation: 5.7.5.4
- C<sub>10</sub>H<sub>25</sub>KSi<sub>2</sub>**  
 $K[(C_2H_5)_3SiSi(C_2H_5)_2]$   
 Formation: 5.5.4.6
- C<sub>10</sub>H<sub>26</sub>Si<sub>2</sub>**  
 $(C_2H_5)_3SiSi(C_2H_5)_2H$   
 Reaction with R<sub>2</sub>Hg: 5.7.3.3
- C<sub>10</sub>H<sub>27</sub>LiSi<sub>3</sub>**  
 $[(CH_3)_3Si]_2CHSi(CH_3)_2CH_2Li$   
 Formation: 5.5.2.3.2  
 $[(CH_3)_3Si]_3CLi$   
 Formation: 5.5.2.3.2, 5.5.2.3.3  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
 Reaction with ZnX<sub>2</sub>: 5.7.2.3.1
- C<sub>10</sub>H<sub>28</sub>AuBrP<sub>2</sub>**  
 $[Au(CH_3)_2(CH_2PMe_3)_2]Br$   
 Formation: 5.6.4.3
- C<sub>10</sub>H<sub>28</sub>Hg<sub>2</sub>Si<sub>4</sub>**  
 $Si(CH_3)_2HgSi(CH_3)_2CH_2Si(CH_3)_2HgSi^*$   
 $(CH_3)_2CH_2$   
 Formation: 5.7.3.2
- C<sub>10</sub>H<sub>30</sub>Si<sub>4</sub>**  
 $(CH_3)_{10}Si_4$   
 Reaction with Na-K: 5.5.4.2.1
- C<sub>11</sub>H<sub>5</sub>Cl<sub>5</sub>Hg**  
 $C_6H_5HgC_5Cl_5-h^1$   
 Formation: 5.7.2.3.4
- C<sub>11</sub>H<sub>9</sub>K**  
 1-Naphthylpotassium  
 Formation: 5.5.3.3.2  
 2-Naphthylpotassium  
 Formation: 5.5.3.3.2
- C<sub>11</sub>H<sub>9</sub>Na**  
 1-Naphthylsodium  
 Formation: 5.5.3.3.2  
 2-Naphthylsodium  
 Formation: 5.5.3.3.2
- C<sub>11</sub>H<sub>10</sub>CILi**  
 $C_6H_5CH=CHC(CH_3)C(Li)Cl$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>10</sub>LiN**  
 $o-C_6H_4C(CH_2Li)=NC(CH_3)=CH$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>11</sub>FeLi**  
 $h^5-C_5H_5FeC_5H_4CH_2Li-h^5$   
 Formation: 5.5.2.2.5
- C<sub>11</sub>H<sub>11</sub>LiMnNO<sub>3</sub>**  
 $(CO)_3Mn[1-Li-2-(CH_3)_2NCH_2C_5H_3-h^5]$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>11</sub>LiN<sub>2</sub>**  
 $[CH_2 \cdots CH \cdots C[NMePhCN]Li]$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>11</sub>LiO**  
 $m-CH_3OC_6H_4CH_2CH_2C \equiv CLi$   
 Formation: 5.5.2.2.2
- C<sub>11</sub>H<sub>11</sub>LiOSe**  
 $C_6H_5Se(O)CH(Li)CH_2C \equiv CCH_3$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>11</sub>LiO<sub>2</sub>**  
 $(E)-C_6H_5CH=C(CO_2C_2H_5)Li$   
 Formation: 5.5.2.3.2  
 $(Z)-C_6H_5CH=C(CO_2C_2H_5)Li$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>11</sub>LiO<sub>2</sub>Se**  
 $C(O)O(CH_2)_3C(Li)SeC_6H_5$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>11</sub>LiS**  
 $(CH_3)_2C=C=C(C_6H_5S)Li$   
 Formation: 5.5.2.3.1
- C<sub>11</sub>H<sub>12</sub>LiNO**  
 $o-LiC_6H_4C=NC(CH_3)_2CH_2O$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>13</sub>Li**  
 $(C_6H_5)(CH_3)CCH_2C(CH_3)Li$   
 Formation: 5.5.2.3.5

- C<sub>11</sub>H<sub>13</sub>LiO<sub>2</sub>**  
p-LiC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.3
- C<sub>11</sub>H<sub>13</sub>LiO<sub>2</sub>S**  
[CH<sub>2</sub>≡C(CH<sub>3</sub>)≡CHSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>13</sub>LiS**  
(CH<sub>3</sub>)<sub>2</sub>CCH<sub>2</sub>C(SC<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.3.5  
[(CH<sub>3</sub>)<sub>2</sub>C≡CH≡CHSC<sub>6</sub>H<sub>5</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2  
C<sub>6</sub>H<sub>5</sub>SC(Li)C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>  
Formation: 5.5.2.2.5
- C<sub>11</sub>H<sub>13</sub>Li<sub>2</sub>N**  
(CH<sub>3</sub>)<sub>3</sub>CC(Li)=NC<sub>6</sub>H<sub>4</sub>Li-o  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>13</sub>Li<sub>2</sub>NO**  
o-LiC<sub>6</sub>H<sub>4</sub>NLiOC(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>13</sub>Li<sub>2</sub>NO<sub>2</sub>**  
o-LiC<sub>6</sub>H<sub>4</sub>NLiCO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>13</sub>Li<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S**  
p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N(Li)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(Li)\*  
NC  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>14</sub>F<sub>3</sub>LiSeSi**  
m-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SeCHLiSi(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>14</sub>HgO<sub>2</sub>**  
p-i-C<sub>3</sub>H<sub>7</sub>C<sub>6</sub>H<sub>4</sub>HgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.7
- C<sub>11</sub>H<sub>14</sub>LiNO**  
o-LiC<sub>6</sub>H<sub>4</sub>CON(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>14</sub>LiNOSi**  
C<sub>6</sub>H<sub>5</sub>C(Li)CN[OSi(CH<sub>3</sub>)<sub>3</sub>]  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>14</sub>LiNS**  
C<sub>6</sub>H<sub>5</sub>SC(Li)=CHCH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>14</sub>Li<sub>2</sub>O**  
LiCH<sub>2</sub>CH(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)CH(CH<sub>3</sub>)OLi  
Formation: 5.5.2.3.4
- C<sub>11</sub>H<sub>14</sub>O**  
CH<sub>3</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>OC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>11</sub>H<sub>14</sub>OS**  
CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OCHSC<sub>6</sub>H<sub>5</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>11</sub>H<sub>15</sub>K**  
K[C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]  
Formation: 5.5.3.3.3
- C<sub>11</sub>H<sub>15</sub>LiN<sub>2</sub>**  
o-LiC<sub>6</sub>H<sub>4</sub>CHN(CH<sub>3</sub>)(CH<sub>2</sub>)<sub>2</sub>NCH<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>15</sub>LiO<sub>2</sub>**  
C<sub>2</sub>H<sub>5</sub>CH(Li)OCH<sub>2</sub>OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1  
LiCH(C<sub>6</sub>H<sub>5</sub>)OCH(CH<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1
- C<sub>11</sub>H<sub>15</sub>LiS**  
CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH(SC<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.2.5  
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(SC<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.2.5, 5.5.2.3.5
- C<sub>11</sub>H<sub>15</sub>LiSe**  
C<sub>6</sub>H<sub>5</sub>SeCH(Li)CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.4
- C<sub>11</sub>H<sub>16</sub>OS**  
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH(OCH<sub>3</sub>)SC<sub>6</sub>H<sub>5</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>11</sub>H<sub>16</sub>S**  
CH<sub>3</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>11</sub>H<sub>16</sub>SSn**  
(CH<sub>3</sub>)<sub>3</sub>SnC[S(C<sub>6</sub>H<sub>5</sub>)]≡CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>11</sub>H<sub>17</sub>LiSn**  
CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)CHCH<sub>2</sub>(CH<sub>3</sub>)CH<sub>3</sub>SnLi  
Formation: 5.5.6.3.1
- C<sub>11</sub>H<sub>18</sub>Cl<sub>2</sub>Hg<sub>2</sub>O<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>CC(O)]<sub>2</sub>C(HgCl)<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>11</sub>H<sub>18</sub>SSi**  
(CH<sub>3</sub>)<sub>3</sub>SiCH(CH<sub>3</sub>)SC<sub>6</sub>H<sub>5</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>11</sub>H<sub>19</sub>ClHgO<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>CC(O)]<sub>2</sub>CHHgCl  
Formation: 5.7.2.3.2, 5.7.2.3.4
- C<sub>11</sub>H<sub>19</sub>Li**  
n-C<sub>8</sub>H<sub>17</sub>CH=C=CHLi  
Formation: 5.5.2.3.3  
2-Butylnorboran-3-yllithium  
Formation: 5.5.2.3.4
- C<sub>11</sub>H<sub>19</sub>LiN<sub>2</sub>O**  
(E)-CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NCLi≡C[C(O)N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]  
H<sub>3</sub>)<sub>2</sub>]H  
Formation: 5.5.2.3.2

- C<sub>11</sub>H<sub>19</sub>LiO<sub>2</sub>S**  
 $\text{CH}(\text{C}_3\text{H}_7\text{-i-trans})\text{CH}_2\text{CH}_2\text{CH}^*$   
 $(\text{CH}_3\text{cis})\text{CHOC}(\text{O})\text{SCH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>20</sub>CuP**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Cu} \cdot \text{PEt}_3$   
 Formation: 5.6.4.3
- C<sub>11</sub>H<sub>21</sub>Li**  
 $\text{LiCH}(\text{CH}_2)_5\text{CHC}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.4
- C<sub>11</sub>H<sub>21</sub>LiN<sub>2</sub>S<sub>4</sub>**  
 $[(\text{C}_2\text{H}_5)_2\text{NC}(\text{S})\text{S}]_2\text{CHLi}$   
 Formation: 5.5.2.3.2
- C<sub>11</sub>H<sub>21</sub>LiO<sub>2</sub>**  
 $\text{CH}_3(\text{CH}_2)_3\text{OC}(\text{Li})=\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{C}^*\text{H}_3$   
 Formation: 5.5.2.3.2  
 $\text{LiCH}(\text{cyclo-C}_6\text{H}_{11})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.1
- C<sub>11</sub>H<sub>22</sub>Sn**  
 $(\text{CH}_3)_3\text{SnCH}_2\text{CH}=\text{C}(\text{CH}_2)_4\text{CH}_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>11</sub>H<sub>23</sub>ClHgO**  
 $(\text{CH}_3)_3\text{CCH}(\text{OCH}_3)\text{CH}(\text{HgCl})\text{C}(\text{CH}_3)_3$   
 Formation: 5.7.2.3.3
- C<sub>11</sub>H<sub>23</sub>HgNO<sub>4</sub>**  
 $\text{n-C}_8\text{H}_{17}\text{CH}(\text{OCH}_3)\text{CH}_2\text{HgNO}_3$   
 Formation: 5.7.2.3.3
- C<sub>11</sub>H<sub>23</sub>HgNSi<sub>2</sub>**  
 $\text{C}_5\text{H}_5\text{HgN}[\text{Si}(\text{CH}_3)_3]_2$   
 Formation: 5.7.2.3.2
- C<sub>11</sub>H<sub>23</sub>Li**  
 $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{Li})\text{CH}_2\text{CH}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.4  
 $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>11</sub>H<sub>23</sub>LiOSi**  
 $(\text{E})\text{-LiCH}=\text{CHCH}(\text{C}_5\text{H}_{11})\text{OSi}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.1
- C<sub>11</sub>H<sub>23</sub>LiO<sub>2</sub>**  
 $\text{LiCH}(\text{C}_6\text{H}_{13})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.1
- C<sub>11</sub>H<sub>24</sub>Sn<sub>2</sub>**  
 $\text{Me}_3\text{SnCH}=\text{CHCH}_2\text{CH}=\text{CHSnMe}_3$   
 Reaction with RLi: 5.5.2.3.1
- C<sub>11</sub>H<sub>27</sub>NSi**  
 $(\text{CH}_3)_3\text{SiN}(\text{n-C}_4\text{H}_9)_2$   
 Formation: 5.5.6
- C<sub>12</sub>BrF<sub>10</sub>Tl**  
 $\text{Tl}(\text{C}_6\text{F}_5)_2\text{Br}$   
 Reaction with LAuR: 5.6.4.1
- C<sub>12</sub>Br<sub>2</sub>F<sub>8</sub>Hg**  
 $(\text{o-BrC}_6\text{F}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>Br<sub>8</sub>Cl<sub>2</sub>Hg**  
 $(\text{p-ClC}_6\text{Br}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7
- C<sub>12</sub>Br<sub>8</sub>F<sub>2</sub>Hg**  
 $(\text{p-FC}_6\text{Br}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7
- C<sub>12</sub>Br<sub>10</sub>Hg**  
 $(\text{C}_6\text{Br}_5)_2\text{Hg}$   
 Formation: 5.7.2.3.7  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.2
- C<sub>12</sub>CdF<sub>10</sub>**  
 $(\text{C}_6\text{F}_5)_2\text{Cd}$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>Cl<sub>8</sub>HgN<sub>2</sub>O<sub>4</sub>**  
 $(\text{p-NO}_2\text{C}_6\text{Cl}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.4
- C<sub>12</sub>Cl<sub>10</sub>Hg**  
 $(\text{C}_6\text{Cl}_5)_2\text{Hg}$   
 Formation: 5.7.2.3.1, 5.7.2.3.4, 5.7.2.3.7  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.2
- C<sub>12</sub>CuF<sub>10</sub>Li**  
 $(\text{C}_6\text{F}_5)_2\text{CuLi}$   
 Formation: 5.6.4.3
- C<sub>12</sub>D<sub>10</sub>Hg**  
 $(\text{C}_6\text{D}_5)_2\text{Hg}$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>F<sub>8</sub>HgN<sub>2</sub>O<sub>4</sub>**  
 $[\text{2-C}_5\text{F}_4\text{NC}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7
- C<sub>12</sub>F<sub>10</sub>Hg**  
 $(\text{C}_6\text{F}_5)_2\text{Hg}$   
 Formation: 5.7.2.2.1, 5.7.2.3.1, 5.7.2.3.4, 5.7.2.3.7  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.2  
 Reaction with  $\text{Hg}(\text{N}_3)_2$ : 5.7.2.3.2
- C<sub>12</sub>F<sub>10</sub>Zn**  
 $(\text{C}_6\text{F}_5)_2\text{Zn}$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.2
- C<sub>12</sub>HBrF<sub>10</sub>Ge**  
 $(\text{C}_6\text{F}_5)_2\text{GeBrH}$   
 Reaction with  $\text{R}_2\text{Hg}$ : 5.7.4.2
- C<sub>12</sub>H<sub>2</sub>Cl<sub>8</sub>Hg**  
 $(\text{m-HC}_6\text{Cl}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7  
 $(\text{o-HC}_6\text{Cl}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7  
 $(\text{p-HC}_6\text{Cl}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7

- C<sub>12</sub>H<sub>2</sub>F<sub>8</sub>Hg**  
 (m- $\text{HC}_6\text{F}_4$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.7  
 (o- $\text{HC}_6\text{F}_4$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.7  
 (p- $\text{HC}_6\text{F}_4$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>2</sub>F<sub>8</sub>HgO<sub>3</sub>S**  
 m- $\text{HC}_6\text{F}_4\text{HgO}_3\text{SC}_6\text{F}_4\text{H-m}$   
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>4</sub>Cl<sub>6</sub>Hg**  
 (2,3,4- $\text{Cl}_3\text{C}_6\text{H}_2$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.4, 5.7.2.3.7
- C<sub>12</sub>H<sub>4</sub>Cl<sub>10</sub>HgO<sub>8</sub>S<sub>2</sub>**  
 (C<sub>6</sub>Cl<sub>5</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7
- C<sub>12</sub>H<sub>4</sub>F<sub>10</sub>HgO<sub>8</sub>S<sub>2</sub>**  
 (C<sub>6</sub>F<sub>5</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7
- C<sub>12</sub>H<sub>4</sub>HgN<sub>6</sub>O<sub>12</sub>**  
 [2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>Hg  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>5</sub>Br<sub>5</sub>Hg**  
 C<sub>6</sub>H<sub>5</sub>HgC<sub>6</sub>Br<sub>5</sub>  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>5</sub>Cl<sub>5</sub>Hg**  
 C<sub>6</sub>H<sub>5</sub>HgC<sub>6</sub>Cl<sub>5</sub>  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>5</sub>F<sub>5</sub>Hg**  
 C<sub>6</sub>H<sub>5</sub>HgC<sub>6</sub>F<sub>5</sub>  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>5</sub>F<sub>9</sub>Si**  
 C<sub>6</sub>H<sub>5</sub>Si(CF=CF<sub>2</sub>)<sub>3</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>12</sub>H<sub>6</sub>Cl<sub>4</sub>Hg**  
 (3,4- $\text{Cl}_2\text{C}_6\text{H}_3$ )<sub>2</sub>Hg  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>12</sub>H<sub>6</sub>Cl<sub>8</sub>HgO<sub>8</sub>S<sub>2</sub>**  
 (m- $\text{HC}_6\text{Cl}_4\text{SO}_3$ )<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7  
 (o- $\text{HC}_6\text{Cl}_4\text{SO}_3$ )<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7  
 (p- $\text{HC}_6\text{Cl}_4\text{SO}_3$ )<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7
- C<sub>12</sub>H<sub>6</sub>F<sub>4</sub>Hg**  
 (2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>Hg  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>6</sub>F<sub>8</sub>HgO<sub>8</sub>S<sub>2</sub>**  
 (m- $\text{HC}_6\text{F}_4\text{SO}_3$ )<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7  
 (o- $\text{HC}_6\text{F}_4\text{SO}_3$ )<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7
- (p- $\text{HC}_6\text{F}_4\text{SO}_3$ )<sub>2</sub>Hg · 2 OH<sub>2</sub>  
 Desulfonation: 5.7.2.3.7
- C<sub>12</sub>H<sub>6</sub>Li<sub>2</sub>**  
 5,6-Li<sub>2</sub>-Acenaphthene  
 Formation: 5.5.2.3.3
- C<sub>12</sub>H<sub>8</sub>BrLiO<sub>2</sub>S**  
 2-Li-3-C<sub>6</sub>H<sub>3</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Br  
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>8</sub>CdCl<sub>2</sub>**  
 (p- $\text{ClC}_6\text{H}_4$ )<sub>2</sub>Cd  
 Formation: 5.7.2.3.1
- C<sub>12</sub>H<sub>8</sub>ClLiO**  
 2-C<sub>6</sub>H<sub>5</sub>O-5- $\text{ClC}_6\text{H}_3$ Li  
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>Hg**  
 (ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg  
 Reaction with Zn metal: 5.7.2.2.2
- C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>HgO<sub>2</sub>S**  
 p- $\text{ClC}_6\text{H}_4\text{HgO}_2\text{SC}_6\text{H}_4\text{Cl-p}$   
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>Zn**  
 (ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Zn  
 Formation: 5.7.2.2.2
- C<sub>12</sub>H<sub>8</sub>F<sub>2</sub>Hg**  
 (FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg  
 Reaction with Zn metal: 5.7.2.2.2
- (p- $\text{FC}_6\text{H}_4$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>8</sub>F<sub>2</sub>HgO<sub>4</sub>S<sub>2</sub>**  
 (p- $\text{FC}_6\text{H}_4\text{SO}_2$ )<sub>2</sub>Hg  
 Desulfination: 5.7.2.3.7
- C<sub>12</sub>H<sub>8</sub>F<sub>2</sub>Zn**  
 (FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Zn  
 Formation: 5.7.2.2.2
- C<sub>12</sub>H<sub>8</sub>Hg**  
 2,2'-(C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>)Hg  
 Reaction with Li metal: 5.5.2.2.2
- C<sub>12</sub>H<sub>8</sub>HgI<sub>2</sub>**  
 (p- $\text{IC}_6\text{H}_4$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.6
- C<sub>12</sub>H<sub>8</sub>HgN<sub>2</sub>O<sub>4</sub>**  
 (o- $\text{NO}_2\text{C}_6\text{H}_4$ )<sub>2</sub>Hg  
 Formation: 5.7.2.3.7
- C<sub>12</sub>H<sub>8</sub>Li**  
 Li biphenylene radical anion  
 Formation: 5.5.2.2.3
- C<sub>12</sub>H<sub>8</sub>Li<sub>2</sub>**  
 2,2'-LiC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Li  
 Reaction with CdX<sub>2</sub>: 5.7.2.3.1  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
 Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.2.3
- C<sub>12</sub>H<sub>8</sub>Li<sub>2</sub>O**  
 2,2'-LiOC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Li  
 Formation: 5.5.2.3.2, 5.5.2.2.5

- C<sub>12</sub>H<sub>8</sub>Li<sub>2</sub>O<sub>2</sub>S**  
(o-LiC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>8</sub>Li<sub>2</sub>S**  
2,2'-LiSC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.5
- C<sub>12</sub>H<sub>8</sub>O**  
Dibenzofuran  
Reaction with Li metal: 5.5.2.2.5
- C<sub>12</sub>H<sub>8</sub>S**  
Dibenzothiophene  
Reaction with Li metal: 5.5.2.2.5
- C<sub>12</sub>H<sub>9</sub>CHg**  
o-(C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>HgCl  
Formation: 5.7.2.3.6
- C<sub>12</sub>H<sub>9</sub>Li**  
m-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1  
o-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.2.2, 5.5.2.3.4  
p-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.3.1
- C<sub>12</sub>H<sub>9</sub>LiN<sub>4</sub>**  
2,5-(CH=CHCH=NN)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Li  
Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>9</sub>LiO**  
o-LiC<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>9</sub>LiO<sub>2</sub>S**  
o-LiC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>10</sub>AsLi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>AsLi  
Formation: 5.5.2.2.5
- C<sub>12</sub>H<sub>10</sub>AuClZn**  
AuZnCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.6.4.1
- C<sub>12</sub>H<sub>10</sub>Au<sub>2</sub>Cl<sub>4</sub>**  
(C<sub>6</sub>H<sub>5</sub>AuCl<sub>2</sub>)<sub>2</sub>  
Formation: 5.6.4.3  
Reaction with Ph<sub>2</sub>Zn: 5.6.4.1
- C<sub>12</sub>H<sub>10</sub>Br<sub>2</sub>Ge**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>GeBr<sub>2</sub>  
Formation: 5.7.4.2
- C<sub>12</sub>H<sub>10</sub>Cd**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cd  
Formation: 5.7.2.2.2, 5.7.2.3.1  
Reaction with CdX<sub>2</sub>: 5.7.2.3.2  
Reaction with C<sub>6</sub>H<sub>5</sub>Li: 5.7.2.4.3
- C<sub>12</sub>H<sub>10</sub>Cl<sub>2</sub>Pb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PbCl<sub>2</sub>  
Reaction with Li metal: 5.5.7.4
- C<sub>12</sub>H<sub>10</sub>Cl<sub>2</sub>Sn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnCl<sub>2</sub>  
Reaction with Li metal: 5.5.6.3.1
- C<sub>12</sub>H<sub>10</sub>Cs<sub>2</sub>**  
Cs<sub>2</sub>[C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>]  
Formation: 5.5.3.2.4
- C<sub>12</sub>H<sub>10</sub>FeLiN**  
h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(C<sub>5</sub>H<sub>4</sub>CHLiCN)-h<sup>5</sup>  
Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>10</sub>GeLi<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>GeLi<sub>2</sub>  
Formation: 5.5.5.4
- C<sub>12</sub>H<sub>10</sub>GeNa<sub>2</sub>**  
Na<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Ge]  
Formation: 5.5.5.2.1, 5.5.5.2.2
- C<sub>12</sub>H<sub>10</sub>Hg**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.2.1, 5.7.2.3.6, 5.7.2.3.7  
Metal exchange with NaR: 5.5.3.3.2  
Reaction with Cd metal: 5.7.2.2.2  
Reaction with Hg(O<sub>2</sub>SPh)<sub>2</sub>: 5.7.2.3.2  
Reaction with Hg(NO<sub>3</sub>)<sub>2</sub>: 5.7.2.3.2  
Reaction with Zn metal: 5.7.2.2.2  
Reaction with Li metal: 5.5.2.2.2  
Transmetallation: 5.5.2.3.1
- C<sub>12</sub>H<sub>10</sub>HgO<sub>2</sub>**  
2-C<sub>10</sub>H<sub>7</sub>HgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.4
- C<sub>12</sub>H<sub>10</sub>HgO<sub>2</sub>S**  
C<sub>6</sub>H<sub>5</sub>Hg(O<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>)  
Formation: 5.7.2.3.2
- C<sub>12</sub>H<sub>10</sub>HgO<sub>4</sub>S<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>Hg  
Desulfination: 5.7.2.3.7
- C<sub>12</sub>H<sub>10</sub>K**  
[C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>]<sup>-</sup>K<sup>+</sup>  
Formation: 5.5.3.2.4
- C<sub>12</sub>H<sub>10</sub>K<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>C(K)CH=CHCH(K)CH=CH  
Formation: 5.5.3.3.3  
[C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>]<sup>2-</sup>·2K<sup>+</sup>  
Formation: 5.5.3.2.4
- C<sub>12</sub>H<sub>10</sub>Li**  
[C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>5</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.2.3  
Lithiating: 5.5.2.3.5  
Reaction with anisole: 5.5.3.2.2  
Li heptalene radical anion  
Formation: 5.5.2.2.3
- C<sub>12</sub>H<sub>10</sub>LiN**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NLi  
Formation: 5.5.2.2.5

- C<sub>12</sub>H<sub>10</sub>LiN<sub>4</sub>**  
 $\overline{\text{p}(\text{CHLi}=\text{CHCH}=\text{NN})\text{C}_6\text{H}_4(\text{N}=\text{CHC}^*\text{H}=\text{CH})}$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>10</sub>LiP**  
 $(\text{C}_6\text{H}_5)_2\text{PLi}$   
 Formation: 5.5.2.2.5
- C<sub>12</sub>H<sub>10</sub>LiSb**  
 $(\text{C}_6\text{H}_5)_2\text{SbLi}$   
 Formation: 5.5.2.2.5
- C<sub>12</sub>H<sub>10</sub>Li<sub>2</sub>**  
 $[\text{C}_6\text{H}_5\text{C}_6\text{H}_5]^{2-} \cdot 2 \text{Li}^+$   
 Formation: 5.5.2.2.3  
 dilithioheptalene  
 Formation: 5.5.2.2.3
- C<sub>12</sub>H<sub>10</sub>Li<sub>2</sub>Pb**  
 $(\text{C}_6\text{H}_5)_2\text{PbLi}_2$   
 Reaction with RBr: 5.5.7.4
- C<sub>12</sub>H<sub>10</sub>Li<sub>2</sub>Sn**  
 $(\text{C}_6\text{H}_5)_2\text{SnLi}_2$   
 Formation: 5.5.6.3.1
- C<sub>12</sub>H<sub>10</sub>Na**  
 $[\text{C}_6\text{H}_5\text{C}_6\text{H}_5]^- \cdot \text{Na}^+$   
 Formation: 5.5.3.2.4
- C<sub>12</sub>H<sub>10</sub>Na<sub>2</sub>Sn**  
 $\text{Na}_2[(\text{C}_6\text{H}_5)_2\text{Sn}]$   
 Formation: 5.5.6.2.2
- C<sub>12</sub>H<sub>10</sub>Pb**  
 $(\text{C}_6\text{H}_5)_2\text{Pb}$   
 Formation: 5.5.7.5
- C<sub>12</sub>H<sub>10</sub>Rb**  
 $[\text{C}_6\text{H}_5\text{C}_6\text{H}_5]^- \cdot \text{Rb}^+$   
 Formation: 5.5.3.2.4
- C<sub>12</sub>H<sub>10</sub>Sn**  
 $(\text{C}_6\text{H}_5)_2\text{Sn}$   
 Formation: 5.5.6.6
- C<sub>12</sub>H<sub>10</sub>Zn**  
 $(\text{C}_6\text{H}_5)_2\text{Zn}$   
 Formation: 5.7.2.2.2, 5.7.2.3.1  
 Reaction with  $\text{ArC}\equiv\text{CH}$ : 5.7.2.4.1  
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.2  
 Reaction with CuX, AgX, AuX<sub>3</sub>: 5.6.4.1
- C<sub>12</sub>H<sub>11</sub>BrFeHgO**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}(\text{O})\text{CH}_2\text{HgBr}\text{-h}^5$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>H<sub>11</sub>ClFeHg**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}=\text{CHHgCl}\text{-h}^5$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>H<sub>11</sub>ClSi**  
 $(\text{C}_6\text{H}_5)_2\text{HSiCl}$   
 Reaction with Li metal: 5.5.4.2.2, 5.5.4.3
- C<sub>12</sub>H<sub>11</sub>Cl<sub>2</sub>Hg<sub>2</sub>O**  
 $\text{ClHgC}=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5(\text{OCH}_3)\text{C}=\text{CHgCl}$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>H<sub>11</sub>GeLi**  
 $(\text{C}_6\text{H}_5)_2\text{HGeLi}$   
 Formation: 5.5.5.2.1, 5.5.5.2.2
- C<sub>12</sub>H<sub>11</sub>LiSi**  
 $(\text{C}_6\text{H}_5)_2\text{HSiLi}$   
 Formation: 5.5.4.2.1, 5.5.4.2.2, 5.5.4.3
- C<sub>12</sub>H<sub>11</sub>NaSn**  
 $\text{Na}[(\text{C}_6\text{H}_5)_2\text{SnH}]$   
 Formation: 5.5.6.4
- C<sub>12</sub>H<sub>12</sub>Cs<sub>2</sub>**  
 $[\text{HC}(\text{CH}=\text{CH})_2\text{CHCH}(\text{CH}=\text{CH})_2\text{CH}]^* \cdot \text{Cs}_2$   
 Formation: 5.5.3.2.4
- C<sub>12</sub>H<sub>12</sub>Ge**  
 $(\text{C}_6\text{H}_5)_2\text{GeH}_2$   
 Reaction with RLi: 5.5.5.4  
 Reaction with R<sub>2</sub>Hg: 5.7.4.2
- C<sub>12</sub>H<sub>12</sub>Li<sub>2</sub>O**  
 $(\text{LiCH}=\text{CH})_2\text{CC}_6\text{H}_5(\text{OCH}_3)$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>12</sub>H<sub>12</sub>Si**  
 $(\text{C}_6\text{H}_5)_2\text{SiH}_2$   
 Reaction with Li metal: 5.5.4.5  
 Reaction with Na-K: 5.5.4.4
- C<sub>12</sub>H<sub>12</sub>Sn**  
 $(\text{C}_6\text{H}_5)_2\text{SnH}_2$   
 Reaction with R<sub>2</sub>Hg: 5.7.5.2.3
- C<sub>12</sub>H<sub>13</sub>CHgO<sub>2</sub>S**  
 $\overline{\text{CH}_2\text{CH}=\text{CHCH}(\text{SO}_2\text{C}_6\text{H}_5)\text{CH}(\text{HgCl})\text{-H}_2}$   
 Formation: 5.7.2.3.3
- C<sub>12</sub>H<sub>13</sub>FeLi<sub>2</sub>N**  
 $(\text{h}^5\text{-LiC}_5\text{H}_4)\text{Fe}[1\text{-Li-2-}(\text{CH}_3)_2\text{NC}_5\text{H}_3\text{-h}^5]$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>13</sub>LiOS<sub>2</sub>**  
 $[\text{H}_2\text{C}\cdots\text{C}(\text{COC}_6\text{H}_5)\cdots\text{C}(\text{SCH}_3)_2]^- \cdot \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>14</sub>FeLiN**  
 $\text{h}^5\text{C}_5\text{H}_5\text{Fe}[1\text{-Li-2-}(\text{CH}_3)_2\text{NC}_5\text{H}_3\text{-h}^5]$   
 Formation: 5.5.2.3.2  
 $(\text{h}^5\text{-LiC}_5\text{H}_4)\text{Fe}[(\text{CH}_3)_2\text{NC}_5\text{H}_4\text{-h}^5]$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>14</sub>FeO**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{OCH}_3\text{-h}^5$   
 Reaction with Li metal: 5.5.2.2.5
- C<sub>12</sub>H<sub>14</sub>Ge<sub>2</sub>**  
 $\text{H}_2(\text{C}_6\text{H}_5)_2\text{GeGe}(\text{C}_6\text{H}_5)_2$   
 Reaction with Li-Hg: 5.5.5.2.2  
 Reaction with R<sub>2</sub>Hg: 5.7.4.2
- C<sub>12</sub>H<sub>14</sub>Hg**  
 $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.1



- C<sub>12</sub>H<sub>14</sub>LiN**  
 $\text{o-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CHLi}=\text{CN}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.3
- C<sub>12</sub>H<sub>14</sub>LiNO<sub>2</sub>**  
 $2\text{-OCH}_2\text{C}(\text{CH}_3)_2\text{N}=\text{C}-5\text{-CH}_3\text{OC}_6\text{H}_3\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>14</sub>LiNO<sub>2</sub>S**  
 $(\text{E})\text{-C}_6\text{H}_5\text{SC}[\text{N}(\text{CH}_3)_2]=\text{CLiCO}_2\text{CH}_3$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>14</sub>LiOP**  
 $[\text{CH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)\text{CH}\cdots\text{C}(\text{CH}_3)\cdots\text{CCH}_3]^* \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>14</sub>LiPS**  
 $[\text{CH}_2\text{P}(\text{S})(\text{C}_6\text{H}_5)\text{CH}\cdots\text{C}(\text{CH}_3)\cdots\text{CCH}_3]^* \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>14</sub>Br<sub>2</sub>Hg<sub>2</sub>N**  
 $\text{BrHgCH}_2\text{CHN}(\text{Ph})\text{CH}(\text{CH}_2\text{HgBr})\text{CH}_2\text{C}^*\text{H}_2$   
 Formation: 5.7.2.3.3
- C<sub>12</sub>H<sub>15</sub>LiO<sub>2</sub>**  
 $\text{Li}(\text{C}_6\text{H}_5)\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{O}$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>15</sub>Li<sub>2</sub>NO**  
 $\text{o-LiCH}_2\text{C}_6\text{H}_4\text{NLiCOC}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>16</sub>LiNO<sub>2</sub>**  
 $2\text{-Li-3-(C}_2\text{H}_5)_2\text{NCOC}_6\text{H}_3\text{OCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>16</sub>S**  
 $\text{CH}_2(\text{CH}_2)_4\text{CHSC}_6\text{H}_5$   
 Reaction with a Li radical anion:  
 5.5.2.2.5
- C<sub>12</sub>H<sub>17</sub>LiO<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{CHLiOCH}_2\text{OCH}_3$   
 Formation: 5.5.2.3.1
- C<sub>12</sub>H<sub>17</sub>LiO<sub>3</sub>**  
 $\text{LiCH}(\text{C}_6\text{H}_4\text{OCH}_3\text{-m})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.1  
 $\text{LiCH}(\text{C}_6\text{H}_4\text{OCH}_3\text{-p})\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Formation: 5.5.2.3.1
- C<sub>12</sub>H<sub>17</sub>LiS**  
 $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{SC}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.2.2.5  
 $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{CH}_2\text{C}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.4
- C<sub>12</sub>H<sub>17</sub>LiSe**  
 $\text{C}_6\text{H}_5\text{SeCH}(\text{Li})\text{CH}_2\text{C}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.4  
 $\text{C}_6\text{H}_5\text{SeCH}(\text{Li})\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.4
- $\text{C}_6\text{H}_5\text{SeCH}(\text{Li})(\text{CH}_2)_4\text{CH}_3$   
 Formation: 5.5.2.3.2, 5.5.2.3.4
- C<sub>12</sub>H<sub>18</sub>CdO<sub>6</sub>**  
 $\text{Cd}[\text{CH}(\text{COCH}_3)\text{CO}_2\text{C}_2\text{H}_5]_2$   
 Formation: 5.7.2.3.4
- C<sub>12</sub>H<sub>18</sub>Ge<sub>2</sub>**  
 $[(\text{H}_2\text{C}=\text{CH})_3\text{Ge}]_2$   
 Reaction with Li metal: 5.5.5.2.1
- C<sub>12</sub>H<sub>18</sub>Hg**  
 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{C})_2\text{Hg}$   
 Reaction with Li metal: 5.5.2.2.2
- C<sub>12</sub>H<sub>18</sub>HgN<sub>4</sub>O<sub>2</sub>**  
 $\text{Hg}[\text{C}(\text{N}_2)\text{COC}(\text{CH}_3)_3]_2$   
 Formation: 5.7.2.3.4
- C<sub>12</sub>H<sub>18</sub>HgO<sub>2</sub>**  
 $[\text{C}(\text{O})(\text{CH}_2)_4\text{CH}]_2\text{Hg}$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>12</sub>H<sub>18</sub>HgO<sub>6</sub>**  
 $\text{Hg}[\text{CH}(\text{COCH}_3)\text{CO}_2\text{C}_2\text{H}_5]_2$   
 Formation: 5.7.2.3.4
- C<sub>12</sub>H<sub>18</sub>S**  
 $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)\text{SC}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.5
- C<sub>12</sub>H<sub>18</sub>SSi**  
 $(\text{CH}_3)_3\text{SiC}(\text{SC}_6\text{H}_5)\text{CH}_2\text{CH}_2$   
 Reaction with a Li radical anion:  
 5.5.2.2.5
- C<sub>12</sub>H<sub>18</sub>Sn**  
 $(\text{E})\text{-(CH}_3)_3\text{SnCH}_2\text{CH}=\text{CHC}_6\text{H}_5$   
 Transmetalation: 5.5.2.3.1
- C<sub>12</sub>H<sub>18</sub>Sn<sub>2</sub>**  
 $(\text{CH}_2=\text{CH})_3\text{SnSn}(\text{CH}=\text{CH}_2)_3$   
 Reaction with Na naphthalene: 5.5.6.2.2
- C<sub>12</sub>H<sub>19</sub>AuCl<sub>2</sub>S**  
 $\text{C}_6\text{H}_5\text{AuCl}_2\cdot\text{S}(\text{C}_3\text{H}_7\text{-n})_2$   
 Formation: 5.6.4.3
- C<sub>12</sub>H<sub>19</sub>BrGe**  
 $\text{p-(CH}_3\text{CH}_2)_3\text{GeC}_6\text{H}_4\text{Br}$   
 Reaction with Li metal: 5.5.2.2.1
- C<sub>12</sub>H<sub>19</sub>ClSi**  
 $\text{C}_6\text{H}_5(\text{i-C}_3\text{H}_7)_2\text{SiCl}$   
 Reaction with Li metal: 5.5.4.2.2, 5.5.4.3
- C<sub>12</sub>H<sub>19</sub>GeLi**  
 $\text{p-(CH}_3\text{CH}_2)_3\text{GeC}_6\text{H}_4\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>12</sub>H<sub>19</sub>Li<sub>3</sub>OP**  
 $\text{o-C}_6\text{H}_4\text{CH}(\text{Li})\text{N}\{\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2\}\text{CH}_2$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>19</sub>LiSi**  
 $\text{C}_5\text{H}_{11}(\text{C}_6\text{H}_5)\text{CH}_3\text{SiLi}$   
 Formation: 5.5.4.2.1  
 $\text{C}_6\text{H}_5(\text{i-C}_3\text{H}_7)_2\text{SiLi}$   
 Formation: 5.5.4.2.1, 5.5.4.2.2, 5.5.4.3

- C<sub>12</sub>H<sub>20</sub>Ge**  
 $\text{C}_6\text{H}_5\text{Ge}(\text{C}_2\text{H}_5)_3$   
 Formation: 5.5.5.2.2
- C<sub>12</sub>H<sub>20</sub>Li<sub>2</sub>**  
 $\text{LiCH}_2\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{C}^*\text{H}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.3
- C<sub>12</sub>H<sub>20</sub>Pb**  
 $(\text{C}_2\text{H}_5)_3\text{Pb}(\text{C}_6\text{H}_5)$   
 Reaction with Na metal: 5.5.7.3
- C<sub>12</sub>H<sub>20</sub>Si**  
 $(\text{C}_2\text{H}_5)_3\text{SiC}_6\text{H}_5$   
 Formation: 5.5.4.7
- C<sub>12</sub>H<sub>20</sub>Sn**  
 $(\text{CH}_2\text{CH}_2\text{CH})_4\text{Sn}$   
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1  
 Transmetallation: 5.5.2.3.1  
 $(\text{CH}_2=\text{CHCH}_2)_4\text{Sn}$   
 Transmetallation: 5.5.2.3.1  
 $(\text{cis-CH}_3\text{CH}=\text{CH})_4\text{Sn}$   
 Transmetallation: 5.5.2.3.1  
 $(\text{trans-CH}_3\text{CH}=\text{CH})_4\text{Sn}$   
 Transmetallation: 5.5.2.3.1
- C<sub>12</sub>H<sub>21</sub>Hg<sub>2</sub>O<sub>9</sub>P**  
 $[\text{CH}_3\text{C}(\text{O})\text{OHg}]_2\text{C}[(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})]\text{CO}_2^*\text{C}_2\text{H}_5$   
 Formation: 5.7.2.3.4
- C<sub>12</sub>H<sub>21</sub>LiN<sub>3</sub>OP**  
 $[(\text{CH}_3)_2\text{N}]_2\text{P}(\text{O})\text{N}(\text{CH}_3)\text{CH}(\text{Li})\text{C}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>21</sub>LiOSi**  
 $(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{SiOC}=\text{CH}(\text{CH}_2)_2\text{C}^*\text{Li}=\text{CH}$   
 Formation: 5.5.2.3.1
- C<sub>12</sub>H<sub>22</sub>Cd**  
 $(\text{cyclo-C}_6\text{H}_{11})_2\text{Cd}$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>12</sub>H<sub>22</sub>Hg**  
 $(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2)_2\text{Hg}$   
 Reaction with Li metal: 5.5.2.2.2
- C<sub>12</sub>H<sub>22</sub>Na<sub>2</sub>Sn**  
 $\text{Na}_2[(\text{cyclo-C}_6\text{H}_{11})_2\text{Sn}]$   
 Formation: 5.5.6.2.2
- C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>**  
 $\text{CH}_3\text{OC}(\text{O})(\text{CH}_2)_8\text{CH}=\text{CH}_2$   
 Reaction with  $\text{Hg}(\text{NO}_3)_2$ : 5.7.2.3.3
- C<sub>12</sub>H<sub>22</sub>Sn<sub>2</sub>**  
 $\text{o-}[(\text{CH}_3)_3\text{Sn}]_2\text{C}_6\text{H}_4$   
 Reaction with RLi: 5.5.2.3.1
- C<sub>12</sub>H<sub>23</sub>B**  
 $[\text{CH}_2(\text{CH}_2)_4\text{CH}]_2\text{BH}$   
 Hydroboration reagent: 5.7.2.3.1
- C<sub>12</sub>H<sub>23</sub>Br**  
 $\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CHBr}$   
 Reaction with K or Na metal: 5.5.3.2.1
- C<sub>12</sub>H<sub>23</sub>K**  
 $[\text{CH}_3(\text{CH}_2)_8\text{CH}\cdots\text{CH}\cdots\text{CH}_2]^\cdot\text{K}^+$   
 Formation: 5.5.3.2.1  
 $\text{K}[\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}]$   
 Formation: 5.5.3.2.1
- C<sub>12</sub>H<sub>23</sub>LiSi<sub>3</sub>**  
 $[(\text{CH}_3)_3\text{Si}]_2\text{Si}(\text{C}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.4.5
- C<sub>12</sub>H<sub>23</sub>Na**  
 $[\text{CH}_3(\text{CH}_2)_8\text{CH}\cdots\text{CH}\cdots\text{CH}_2]^\cdot\text{Na}^+$   
 Formation: 5.5.3.2.1
- C<sub>12</sub>H<sub>23</sub>Na<sub>2</sub>**  
 $\text{Na}[\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}]\text{Na}$   
 Formation: 5.5.3.2.1
- C<sub>12</sub>H<sub>24</sub>O<sub>3</sub>Si**  
 $(\text{CH}_3)_3\text{SiC}\equiv\text{CC}(\text{OC}_2\text{H}_5)_3$   
 Reaction with RLi: 5.5.2.3.1
- C<sub>12</sub>H<sub>24</sub>Sn**  
 $(\text{C}_6\text{H}_{11})_2\text{SnH}_2$   
 Reaction with  $\text{R}_2\text{Hg}$ : 5.7.5.2.3
- C<sub>12</sub>H<sub>25</sub>CHg**  
 $\text{C}_{12}\text{H}_{25}\text{HgCl}$   
 Formation: 5.7.2.3.7  
 $\text{n-C}_{12}\text{H}_{25}\text{HgCl}$   
 Formation: 5.7.2.3.1
- C<sub>12</sub>H<sub>25</sub>K**  
 $\text{K}[\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2]$   
 Formation: 5.5.3.3.2
- C<sub>12</sub>H<sub>25</sub>Li**  
 $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{Li})\text{CH}_2\text{C}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.4  
 $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1  
 Substrate in metal-metal exchange: 5.5.3.3.2
- C<sub>12</sub>H<sub>25</sub>LiOSi**  
 $\text{LiCH}=\text{CHCH}_2\text{C}(\text{CH}_3)(\text{n-C}_4\text{H}_9)\text{OSi}(\text{C}^*\text{H}_3)_3$   
 Formation: 5.5.2.3.1
- C<sub>12</sub>H<sub>26</sub>Sn**  
 $\text{C}_6\text{H}_{13}\text{CH}=\text{CHCH}_2\text{Sn}(\text{CH}_3)_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>12</sub>H<sub>27</sub>B**  
 $(\text{n-C}_4\text{H}_9)_3\text{B}$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- C<sub>12</sub>H<sub>27</sub>BrSi**  
 $[(\text{CH}_3)_3\text{C}]_3\text{SiBr}$   
 Reaction with Na metal: 5.5.4.3

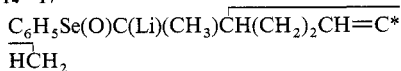
- C<sub>12</sub>H<sub>27</sub>GeNa**  
Na[(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>Ge]  
Formation: 5.5.5.4
- C<sub>12</sub>H<sub>27</sub>LiO<sub>2</sub>Si<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>C(Li)CO<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>12</sub>H<sub>27</sub>LiSi**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SiLi  
Formation: 5.5.4.2.1
- C<sub>12</sub>H<sub>27</sub>LiSn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnLi  
Formation: 5.5.6, 5.5.6.2.1, 5.5.6.3.1
- C<sub>12</sub>H<sub>27</sub>NaSi**  
Na[[CH(CH<sub>3</sub>)<sub>3</sub>C]<sub>3</sub>Si]  
Formation: 5.5.4.3
- C<sub>12</sub>H<sub>27</sub>NaSn**  
Na[(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6.2.2  
Na[(s-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6.2.2
- C<sub>12</sub>H<sub>28</sub>Ge**  
(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>GeH  
Reaction with KH or NaH: 5.5.5.4
- C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Sn**  
(C<sub>2</sub>H<sub>5</sub>OCH<sub>2</sub>)<sub>4</sub>Sn  
Transmetallation: 5.5.2.3.1
- C<sub>12</sub>H<sub>28</sub>Si**  
[(CH<sub>3</sub>)<sub>3</sub>C]<sub>3</sub>SiH  
Reaction with R<sub>2</sub>Cd: 5.7.3.3  
Reaction with R<sub>2</sub>Hg: 5.7.3.3
- C<sub>12</sub>H<sub>28</sub>Sn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3  
Reaction with R<sub>2</sub>NLi: 5.5.6  
(t-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3
- C<sub>12</sub>H<sub>29</sub>LiSi<sub>2</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>C(Li)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.4  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>C(Li)CH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.4  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>C(Li)(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>12</sub>H<sub>30</sub>CdGe<sub>2</sub>**  
[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Cd  
Formation: 5.7.4.2  
Reaction with Hg metal: 5.7.4.4
- C<sub>12</sub>H<sub>30</sub>CdSi<sub>2</sub>**  
[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Si]<sub>2</sub>Cd  
Formation: 5.7.3.3  
Reaction with HgX<sub>2</sub>: 5.7.3.5
- C<sub>12</sub>H<sub>30</sub>GeHgSi**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiHgGe(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Formation: 5.7.4.2
- C<sub>12</sub>H<sub>30</sub>Ge<sub>2</sub>**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>GeGe(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Formation: 5.5.5.2.2  
Reaction with KOEt: 5.5.5.2.2  
Reaction with PhLi: 5.5.5.2.2  
Reaction with K metal: 5.5.5.2.1, 5.5.5.2.2
- C<sub>12</sub>H<sub>30</sub>Ge<sub>2</sub>Hg**  
[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Hg  
Formation: 5.7.4.2, 5.7.4.4  
Reaction with Ph<sub>3</sub>SnBr: 5.7.5.3  
Reaction with R<sub>3</sub>GeBr: 5.7.4.6  
Reaction with R<sub>3</sub>GeH: 5.7.4.2  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.6  
Reaction with Hg—carboranes: 5.7.4.6  
Reaction with Li metal: 5.5.5.6
- C<sub>12</sub>H<sub>30</sub>HgSSi<sub>2</sub>**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiHgSSi(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Reaction with Li metal: 5.5.4.6
- C<sub>12</sub>H<sub>30</sub>HgSi<sub>2</sub>**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiSi(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>HgC<sub>2</sub>H<sub>5</sub>  
Formation: 5.7.3.3  
[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Si]<sub>2</sub>Hg  
Formation: 5.7.3.3, 5.7.3.4  
Reaction with Li, Na or K metal: 5.5.4.6  
Reaction with KCN: 5.7.3.5
- C<sub>12</sub>H<sub>30</sub>HgSn<sub>2</sub>**  
[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
Formation: 5.7.5.2.3, 5.7.5.4
- C<sub>12</sub>H<sub>30</sub>Si<sub>2</sub>Zn**  
[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Si]<sub>2</sub>Zn  
Formation: 5.7.3.3
- C<sub>12</sub>H<sub>30</sub>Sn<sub>2</sub>**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SnSn(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Reaction with Na naphthalene: 5.5.6.2.2
- C<sub>12</sub>H<sub>33</sub>GeLiSi<sub>3</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>GeLi  
Formation: 5.5.5.6
- C<sub>12</sub>H<sub>33</sub>Ge<sub>3</sub>Si<sub>3</sub>Tl**  
[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Ge]<sub>3</sub>Tl  
Reaction with Hg metal: 5.7.4.4
- C<sub>12</sub>H<sub>33</sub>LiSi<sub>3</sub>Sn**  
[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>SnLi  
Formation: 5.5.6
- C<sub>12</sub>H<sub>34</sub>Si<sub>3</sub>Sn**  
[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Cd: 5.7.5.2.2
- C<sub>12</sub>H<sub>36</sub>CdN<sub>2</sub>Si<sub>4</sub>**  
Cd[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>  
Reaction with aliphatics: 5.7.2.3.4  
[(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Cd  
Reaction with R<sub>3</sub>SiH: 5.7.3.5

- C<sub>12</sub>H<sub>36</sub>HgN<sub>2</sub>Si<sub>4</sub>**  
 [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Hg  
 Reaction with aliphatics: 5.7.2.3.4  
 Reaction with alkynes: 5.7.2.3.4  
 Reaction with R<sub>3</sub>GeH: 5.7.4.2  
 Reaction with R<sub>2</sub>Hg: 5.7.2.3.2  
 Reaction with R<sub>3</sub>SiH: 5.7.3.5  
 Reaction with R<sub>3</sub>SnH: 5.7.5
- C<sub>12</sub>H<sub>36</sub>N<sub>2</sub>Si<sub>4</sub>Zn**  
 Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>  
 Reaction with aliphatics: 5.7.2.3.4
- C<sub>12</sub>H<sub>36</sub>Si<sub>5</sub>**  
 [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>4</sub>Si  
 Reaction with MeLi—LiBr: 5.5.4.2.2  
 Reaction with Li or Na metal: 5.5.4.2.1
- C<sub>12</sub>H<sub>36</sub>Si<sub>6</sub>**  
 [(CH<sub>3</sub>)<sub>2</sub>Si]<sub>6</sub>  
 Reaction with Na-K: 5.5.4.2.1
- C<sub>12</sub>Li**  
 LiC<sub>12</sub>  
 Formation: 5.5.2.1
- C<sub>13</sub>H<sub>5</sub>Br<sub>5</sub>HgO<sub>2</sub>**  
 C<sub>6</sub>H<sub>5</sub>HgOC(O)C<sub>6</sub>Br<sub>5</sub>  
 Decarboxylation: 5.7.2.3.7
- C<sub>13</sub>H<sub>5</sub>Cl<sub>5</sub>HgO<sub>2</sub>**  
 C<sub>6</sub>H<sub>5</sub>HgOC(O)C<sub>6</sub>Cl<sub>5</sub>  
 Decarboxylation: 5.7.2.3.7
- C<sub>13</sub>H<sub>5</sub>F<sub>5</sub>HgO<sub>2</sub>**  
 C<sub>6</sub>H<sub>5</sub>HgOC(O)C<sub>6</sub>F<sub>5</sub>  
 Decarboxylation: 5.7.2.3.7
- C<sub>13</sub>H<sub>7</sub>Cl<sub>5</sub>Hg**  
 p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>HgC<sub>6</sub>Cl<sub>5</sub>  
 Formation: 5.7.2.3.7
- C<sub>13</sub>H<sub>9</sub>K**  
 K[ $\overline{\text{C}(\text{CH})}_4\text{CCHC}(\text{CH})_4\text{C}$ ]  
 Formation: 5.5.3.2.5
- C<sub>13</sub>H<sub>9</sub>Li**  
 Fluorenyllithium  
 Formation: 5.5.2.2.4  
 9-Li-fluorene  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>Hg**  
 ClHgCCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
 Formation: 5.7.2.3.5
- C<sub>13</sub>H<sub>10</sub>Li**  
 Li fluorene radical anion  
 Formation: 5.5.2.2.3
- C<sub>13</sub>H<sub>10</sub>Li<sub>2</sub>O**  
 C<sub>6</sub>H<sub>5</sub>C(Li)(OLi)C<sub>6</sub>H<sub>5</sub>  
 Formation: 5.5.2.2.3
- C<sub>13</sub>H<sub>10</sub>O**  
 C<sub>6</sub>H<sub>5</sub>C(O)C<sub>6</sub>H<sub>5</sub>  
 Reaction with Li metal: 5.5.2.2.3
- C<sub>13</sub>H<sub>11</sub>Cs**  
 Cs[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH]  
 Formation: 5.5.3.3.1  
 Cs[p-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>]  
 Formation: 5.5.3.3.1
- C<sub>13</sub>H<sub>11</sub>K**  
 K[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH]  
 Formation: 5.5.3.2.5, 5.5.3.2.6, 5.5.3.3.1  
 K[p-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>]  
 Formation: 5.5.3.2.6
- C<sub>13</sub>H<sub>11</sub>Li**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CHLi  
 Formation: 5.5.2.2.1, 5.5.2.2.5, 5.5.2.3.5
- C<sub>13</sub>H<sub>11</sub>LiOSe**  
 C<sub>6</sub>H<sub>5</sub>Se(O)CH(C<sub>6</sub>H<sub>5</sub>)Li  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>11</sub>LiS**  
 C<sub>6</sub>H<sub>5</sub>SCH(C<sub>6</sub>H<sub>5</sub>)Li  
 Formation: 5.5.2.2.5  
 C<sub>6</sub>H<sub>5</sub>SCH(Li)C<sub>6</sub>H<sub>5</sub>  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>11</sub>LiS<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub>CHLi  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>13</sub>H<sub>11</sub>LiSe**  
 C<sub>6</sub>H<sub>5</sub>SeCH(Li)C<sub>6</sub>H<sub>5</sub>  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>11</sub>LiSe<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Se)<sub>2</sub>CHLi  
 Formation: 5.5.2.3.1, 5.5.2.3.2
- C<sub>13</sub>H<sub>11</sub>LiTe<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Te)<sub>2</sub>CHLi  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>11</sub>Na**  
 Na[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH]  
 Formation: 5.5.3.3.1
- C<sub>13</sub>H<sub>11</sub>Rb**  
 Rb[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH]  
 Formation: 5.5.3.3.1
- C<sub>13</sub>H<sub>12</sub>AsLi**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>AsCH<sub>2</sub>Li  
 Formation: 5.5.2.3.1
- C<sub>13</sub>H<sub>12</sub>AsLiO**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>As(O)CH<sub>2</sub>Li  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>12</sub>HgO<sub>2</sub>S**  
 p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Hg(O<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>)  
 Formation: 5.7.2.3.2
- C<sub>13</sub>H<sub>12</sub>LiOP**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)CH<sub>2</sub>Li  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>12</sub>LiP**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>Li  
 Formation: 5.5.2.3.2

- C<sub>13</sub>H<sub>12</sub>LiSb**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SbCH<sub>2</sub>Li  
 Formation: 5.5.2.3.1
- C<sub>13</sub>H<sub>12</sub>S<sub>2</sub>**  
 C<sub>6</sub>H<sub>5</sub>SCCH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
 Reaction with a Li radical anion:  
 5.5.2.2.5
- C<sub>13</sub>H<sub>12</sub>Se<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Se)<sub>2</sub>CH<sub>2</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>13</sub>H<sub>12</sub>Te<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>Te)<sub>2</sub>CH<sub>2</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>13</sub>H<sub>13</sub>ClSi**  
 CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl  
 Reaction with Li metal: 5.5.4.3
- C<sub>13</sub>H<sub>13</sub>ClSnZn**  
 CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnZnCl  
 Formation: 5.7.5.2.1
- C<sub>13</sub>H<sub>13</sub>LiSi**  
 CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiLi  
 Formation: 5.5.4.2.1, 5.5.4.2.2  
 Reaction with (Ph<sub>2</sub>Si)<sub>6</sub>: 5.5.4.2.2  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>SiLi  
 Formation: 5.5.4.2.1, 5.5.4.3
- C<sub>13</sub>H<sub>13</sub>LiSn**  
 CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnLi  
 Formation: 5.5.6.3.1
- C<sub>13</sub>H<sub>13</sub>NaSi**  
 Na[CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]  
 Formation: 5.5.4.2.1
- C<sub>13</sub>H<sub>14</sub>Sn**  
 CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnH  
 Reaction with RZnCl: 5.7.5.2.1  
 Reaction with R<sub>2</sub>Zn · TMED: 5.7.5.2.1
- C<sub>13</sub>H<sub>15</sub>Cs**  
 Cs[HC(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CHCC<sub>6</sub>H<sub>5</sub>]  
 Formation: 5.5.3.2.2
- C<sub>13</sub>H<sub>15</sub>K**  
 K[HC(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CHCC<sub>6</sub>H<sub>5</sub>]  
 Formation: 5.5.3.2.2
- C<sub>13</sub>H<sub>15</sub>LiOS<sub>2</sub>**  
 C<sub>6</sub>H<sub>5</sub>C(O)C(C<sub>2</sub>H<sub>5</sub>)=C(SCH<sub>3</sub>)SCH<sub>2</sub>Li  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>15</sub>LiS**  
 CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>C=C(SC<sub>6</sub>H<sub>5</sub>)Li  
 Formation: 5.5.2.2.5, 5.5.2.3.5
- C<sub>13</sub>H<sub>16</sub>ClFeHgN**  
 h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe[C<sub>5</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)HgCl-o]-h<sup>5</sup>  
 Formation: 5.7.2.3.1
- C<sub>13</sub>H<sub>16</sub>FeLiN**  
 h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe[C<sub>5</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)Li-o]-h<sup>5</sup>  
 Formation: 5.5.2.3.2  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>13</sub>H<sub>16</sub>LiN**  
 o-LiC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>11</sub>  
 Formation: 5.5.2.3.3
- C<sub>13</sub>H<sub>16</sub>LiNO**  
 (E)-CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>NLi=C[C(O)C<sub>6</sub>H<sub>5</sub>]H  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>16</sub>Li<sub>2</sub>O**  
 C<sub>6</sub>H<sub>5</sub>C(Li)(OLi)CH(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>  
 Formation: 5.5.2.2.3  
 Li(C<sub>6</sub>H<sub>5</sub>)C=C[(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]CH<sub>2</sub>OLi  
 Formation: 5.5.2.3.4
- C<sub>13</sub>H<sub>16</sub>O**  
 C<sub>6</sub>H<sub>5</sub>C(O)CH(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>  
 Reaction with Li metal: 5.5.2.2.3
- C<sub>13</sub>H<sub>18</sub>LiPS**  
 cyclo-C<sub>6</sub>H<sub>11</sub>(C<sub>6</sub>H<sub>5</sub>)P(S)CH<sub>2</sub>Li  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>18</sub>Li<sub>2</sub>O**  
 C<sub>6</sub>H<sub>5</sub>(H)C(OLi)CH[(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]CH<sub>2</sub>Li  
 Formation: 5.5.2.3.4  
 C<sub>6</sub>H<sub>5</sub>(H)C(OLi)CH(Li)(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>  
 Formation: 5.5.2.3.4
- C<sub>13</sub>H<sub>20</sub>S**  
 CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH(CH<sub>3</sub>)SC<sub>6</sub>H<sub>5</sub>  
 Reaction with Li metal: 5.5.2.2.5  
 CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
 Reaction with Li metal: 5.5.2.2.5
- C<sub>13</sub>H<sub>22</sub>HgO<sub>4</sub>**  
 [(CH<sub>3</sub>)<sub>3</sub>CCO]<sub>2</sub>CHHgOC(O)CH<sub>3</sub>  
 Formation: 5.7.2.3.4
- C<sub>13</sub>H<sub>23</sub>LiSn**  
 [CH≡CH≡CH≡CH≡CH≡CHSn(C<sub>4</sub>H<sub>9</sub>-\*  
 n)<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>  
 Formation: 5.5.2.3.2
- C<sub>13</sub>H<sub>24</sub>B<sub>4</sub>O<sub>8</sub>**  
 C[BO(CH<sub>2</sub>)<sub>3</sub>O]<sub>4</sub>  
 Reaction with RLi: 5.5.2.3.1
- C<sub>13</sub>H<sub>24</sub>GeHgN<sub>2</sub>**  
 (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>GeHgC(CN)<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
 Formation: 5.7.4.6
- C<sub>13</sub>H<sub>24</sub>Sn**  
 (n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>SnCH=CHCH<sub>2</sub>CH=CH  
 Reaction with RLi: 5.5.2.3.1
- C<sub>13</sub>H<sub>26</sub>Hg<sub>2</sub>O<sub>10</sub>P<sub>2</sub>**  
 [(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)]<sub>2</sub>C[HgOC(O)CH<sub>3</sub>]<sub>2</sub>  
 Formation: 5.7.2.3.4
- C<sub>13</sub>H<sub>28</sub>Cl<sub>2</sub>F<sub>3</sub>NZn**  
 [(i-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N][CF<sub>3</sub>ZnCl<sub>2</sub>]  
 Formation: 5.7.2.2.1

- C<sub>13</sub>H<sub>31</sub>Cl<sub>2</sub>NZn**  
 $[(i\text{-C}_3\text{H}_7)_4\text{N}][\text{CH}_3\text{ZnCl}_2]$   
 Formation: 5.7.2.2.1
- C<sub>13</sub>H<sub>35</sub>LiSi<sub>4</sub>**  
 $[(\text{CH}_3)_3\text{Si}]_3\text{CSi}(\text{CH}_3)_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>Br<sub>8</sub>Cl<sub>2</sub>HgO<sub>4</sub>**  
 $[\text{p-ClC}_6\text{Br}_4\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>Br<sub>8</sub>F<sub>2</sub>HgO<sub>4</sub>**  
 $[\text{p-FC}_6\text{Br}_4\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>Cl<sub>10</sub>HgO<sub>4</sub>**  
 $\text{Hg}[\text{OC}(\text{O})\text{C}_6\text{Cl}_5]_2$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>F<sub>10</sub>HgO<sub>4</sub>**  
 $\text{Hg}[\text{OC}(\text{O})\text{C}_6\text{F}_5]_2$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>H<sub>4</sub>HgN<sub>6</sub>O<sub>16</sub>**  
 $[2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>H<sub>6</sub>Br<sub>8</sub>HgO<sub>2</sub>**  
 $(\text{p-CH}_3\text{OC}_6\text{Br}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7
- C<sub>14</sub>H<sub>6</sub>F<sub>4</sub>HgO<sub>4</sub>**  
 $[2,6\text{-F}_2\text{C}_6\text{H}_3\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>H<sub>6</sub>F<sub>8</sub>HgO<sub>2</sub>**  
 $(\text{p-CH}_3\text{OC}_6\text{F}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.4
- C<sub>14</sub>H<sub>7</sub>Cl<sub>5</sub>HgO<sub>2</sub>**  
 $\text{p-CH}_3\text{C}_6\text{H}_4\text{HgOC}(\text{O})\text{C}_6\text{Cl}_5$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>H<sub>8</sub>HgN<sub>2</sub>O<sub>8</sub>**  
 $[\text{m-NO}_2\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7  
 $[\text{o-NO}_2\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7  
 $[\text{p-NO}_2\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}]_2\text{Hg}$   
 Decarboxylation: 5.7.2.3.7
- C<sub>14</sub>H<sub>10</sub>BrLi**  
 $(\text{C}_6\text{H}_5)_2\text{C}=\text{CBrLi}$   
 Formation: 5.5.2.3.3
- C<sub>14</sub>H<sub>10</sub>F<sub>4</sub>HgO**  
 $\text{C}_6\text{H}_5\text{HgC}_6\text{F}_4\text{OC}_2\text{H}_5\text{-p}$   
 Formation: 5.7.2.3.7
- C<sub>14</sub>H<sub>10</sub>K**  
 $[\text{C}_{14}\text{H}_{10}]^-\text{K}^+$   
 Formation: 5.5.3.2.4
- C<sub>14</sub>H<sub>10</sub>K<sub>2</sub>**  
 $[\text{C}_{14}\text{H}_{10}]^{2-}2\text{K}^+$   
 Formation: 5.5.3.2.4
- C<sub>14</sub>H<sub>10</sub>Li**  
 $[\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5]^-\text{Li}^+$   
 Formation: 5.5.2.2.3  
 Li anthracene radical anion  
 Formation: 5.5.2.2.3  
 Li phenanthrene radical anion  
 Formation: 5.5.2.2.3
- C<sub>14</sub>H<sub>10</sub>Li<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{C}(\text{Li})=\text{C}(\text{Li})\text{C}_6\text{H}_5$   
 Formation: 5.5.2.2.3  
 $[\text{C}_{14}\text{H}_{10}]^{2-}2\text{Li}^+$   
 Stability: 5.5.3.2.4
- C<sub>14</sub>H<sub>10</sub>Li<sub>2</sub>O<sub>4</sub>**  
 $(\text{C}_6\text{H}_5\text{O})_2\text{C}(\text{Li})\text{CO}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>10</sub>Na**  
 $[\text{C}_{14}\text{H}_{10}]^-\text{Na}^+$   
 Formation: 5.5.3.2.4
- C<sub>14</sub>H<sub>10</sub>Na<sub>2</sub>**  
 $[\text{C}_{14}\text{H}_{10}]^{2-}2\text{Na}^+$   
 Formation: 5.5.3.2.4
- C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>Zn**  
 $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}]_2\text{Zn}$   
 Reaction with  $\text{CH}_2\text{N}_2$ : 5.7.2.3.5
- C<sub>14</sub>H<sub>10</sub>Zn**  
 $\text{C}_6\text{H}_5\text{ZnC}\equiv\text{CC}_6\text{H}_5$   
 Formation: 5.7.2.4.1
- C<sub>14</sub>H<sub>11</sub>BrHg**  
 $(\text{C}_6\text{H}_5)_2\text{C}=\text{CHHgBr}$   
 Formation: 5.7.2.3.4
- C<sub>14</sub>H<sub>11</sub>Li**  
 $(\text{Z})\text{-C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.2.3.1
- C<sub>14</sub>H<sub>11</sub>LiOSe**  
 $\text{C}_6\text{H}_5\text{SeCH}(\text{Li})\text{C}(\text{O})\text{C}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>11</sub>LiS**  
 $\text{LiCS}(\text{C}_6\text{H}_5)=\text{CH}(\text{C}_6\text{H}_5)$   
 Formation: 5.5.2.3.1
- C<sub>14</sub>H<sub>11</sub>LiSe**  
 $(\text{E})\text{-LiC}(\text{SeC}_6\text{H}_5)=\text{CHC}_6\text{H}_5$   
 Formation: 5.5.2.3.1
- C<sub>14</sub>H<sub>11</sub>Li<sub>2</sub>NO**  
 $\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{Li})\text{CHLiC}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>Hg**  
 $(\text{o-ClC}_6\text{H}_4\text{CH}_2)_2\text{Hg}$   
 Formation: 5.7.2.3.1
- C<sub>14</sub>H<sub>12</sub>Li**  
 $[\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5]^-\text{Li}^+$   
 Formation: 5.5.2.2.3
- C<sub>14</sub>H<sub>12</sub>LiN**  
 $[\text{CH}_2=\text{N}=\text{C}(\text{C}_6\text{H}_5)_2]^-\text{Li}^+$   
 Formation: 5.5.2.3.2

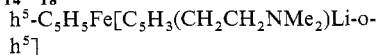
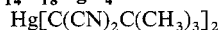
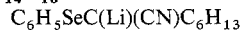
- C<sub>14</sub>H<sub>12</sub>LiN** *contd.*  
 $[\text{C}_6\text{H}_5\text{CH}=\text{N}=\text{CH}(\text{C}_6\text{H}_5)]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>12</sub>Li<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{CH}(\text{Li})\text{C}_6\text{H}_5$   
 Formation: 5.5.2.2.3  
 dilithiooctalene  
 Formation: 5.5.2.2.3
- C<sub>14</sub>H<sub>12</sub>Li<sub>4</sub>**  
 tetralithiooctalene  
 Formation: 5.5.2.2.3
- C<sub>14</sub>H<sub>13</sub>BrHgLiN**  
 $\text{C}_6\text{H}_5\text{N}(\text{Li})\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{HgBr}$   
 Reaction with Li metal: 5.5.2.2.2
- C<sub>14</sub>H<sub>13</sub>K**  
 $\text{K}[\text{C}_6\text{H}_5\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)]$   
 Formation: 5.5.3.2.6
- C<sub>14</sub>H<sub>13</sub>Li**  
 $(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.2.5
- C<sub>14</sub>H<sub>13</sub>LiOSe**  
 $\text{C}_6\text{H}_5\text{Se}(\text{O})\text{CH}(\text{Li})\text{CH}_2\text{C}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>13</sub>LiS**  
 $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{SCH}_2\text{C}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>13</sub>LiS<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{S})_2\text{CLiCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>13</sub>LiSe**  
 $\text{C}_6\text{H}_5\text{SeC}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>13</sub>LiSe<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{Se})_2\text{C}(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.3.1
- C<sub>14</sub>H<sub>13</sub>Li<sub>2</sub>N**  
 $\text{C}_6\text{H}_5\text{N}(\text{Li})\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.2
- C<sub>14</sub>H<sub>13</sub>Na**  
 $[(\text{C}_6\text{H}_5)_2\text{CCH}_3]\text{Na}$   
 Formation: 5.5.3.2.2
- C<sub>14</sub>H<sub>14</sub>AsLiO**  
 $(\text{C}_6\text{H}_5)_2\text{As}(\text{O})\text{CH}(\text{CH}_3)\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>14</sub>Cd**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Cd}$   
 Formation: 5.7.2.3.1
- C<sub>14</sub>H<sub>14</sub>GeLi<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{GeLi}_2$   
 Formation: 5.5.5.5
- C<sub>14</sub>H<sub>14</sub>Hg**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Hg}$   
 Reaction with R<sub>3</sub>SnH: 5.7.5.2.3
- Reaction with Zn metal: 5.7.2.2.2  
 Reaction with Li metal: 5.5.2.2.2  
 Reaction with Na metal: 5.5.3.2.3  
 Transmetalation: 5.5.2.3.1  
 $(\text{o-CH}_3\text{C}_6\text{H}_4)_2\text{Hg}$   
 Reaction with  $\text{Hg}(\text{CNO})_2$ : 5.7.2.3.2  
 $(\text{p-CH}_3\text{C}_6\text{H}_4)_2\text{Hg}$   
 Formation: 5.7.2.3.7  
 Reaction with  $\text{Hg}(\text{O}_2\text{SPh})_2$ : 5.7.2.3.2  
 Reaction with Li metal: 5.5.2.2.2  
 Transmetalation: 5.5.2.3.1
- C<sub>14</sub>H<sub>14</sub>HgO<sub>2</sub>**  
 $(\text{p-CH}_3\text{OC}_6\text{H}_4)_2\text{Hg}$   
 Formation: 5.7.2.2.1
- C<sub>14</sub>H<sub>14</sub>HgO<sub>4</sub>S<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2)_2\text{Hg}$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.2
- C<sub>14</sub>H<sub>14</sub>HgS<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{SCH}_2)_2\text{Hg}$   
 Formation: 5.7.2.3.1  
 Reaction with Zn metal: 5.7.2.2.2  
 Reaction with Li metal: 5.5.2.2.2
- C<sub>14</sub>H<sub>14</sub>LiNO<sub>3</sub>S<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{S}(\text{O})(=\text{NSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-p})\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>14</sub>LiOP**  
 $(\text{C}_6\text{H}_5)_2\text{PCH}(\text{Li})\text{OCH}_3$   
 Formation: 5.5.2.3.2
- C<sub>14</sub>H<sub>14</sub>OSe<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{Se})_2\text{CHOCH}_3$   
 Transmetalation: 5.5.2.3.1
- C<sub>14</sub>H<sub>14</sub>S**  
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.5
- C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{SCH}(\text{CH}_3)\text{SC}_6\text{H}_5$   
 Reaction with a Li radical anion: 5.5.2.2.5
- C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>Zn**  
 $(\text{C}_6\text{H}_5\text{SCH}_2)_2\text{Zn}$   
 Formation: 5.7.2.2.2
- C<sub>14</sub>H<sub>14</sub>Zn**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Zn}$   
 Formation: 5.7.2.3.1, 5.7.2.4.3  
 $(3\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Zn}$   
 Reaction with  $\text{ZnX}_2$ : 5.7.2.3.2  
 $(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Zn}$   
 Formation: 5.7.2.4.3
- C<sub>14</sub>H<sub>15</sub>NaSn**  
 $\text{Na}[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnH}]$   
 Formation: 5.5.6.4

**C<sub>14</sub>H<sub>17</sub>LiOSe**

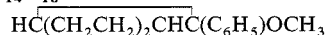
Formation: 5.5.2.3.2

**C<sub>14</sub>H<sub>17</sub>LiS**

Formation: 5.5.2.2.5

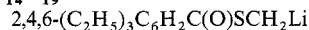
**C<sub>14</sub>H<sub>18</sub>FeLiN**Reaction with HgX<sub>2</sub>: 5.7.2.3.1**C<sub>14</sub>H<sub>18</sub>HgN<sub>4</sub>**Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.6**C<sub>14</sub>H<sub>18</sub>LiNSe**

Formation: 5.5.2.3.2

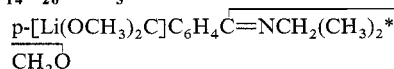
**C<sub>14</sub>H<sub>18</sub>O**Reaction with Na-K or Cs-K-Na:  
5.5.3.2.2**C<sub>14</sub>H<sub>19</sub>Li**

1-Lithiobiadamantane

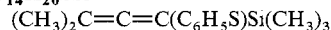
Formation: 5.5.2.2.1

**C<sub>14</sub>H<sub>19</sub>LiOS**

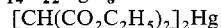
Formation: 5.5.2.3.2

**C<sub>14</sub>H<sub>20</sub>LiNO<sub>3</sub>**

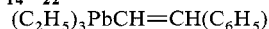
Formation: 5.5.2.3.2

**C<sub>14</sub>H<sub>20</sub>SSi**

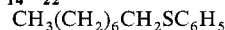
Reaction with RLi: 5.5.2.3.1

**C<sub>14</sub>H<sub>22</sub>HgO<sub>8</sub>**

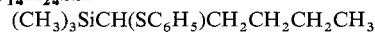
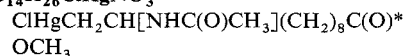
Formation: 5.7.2.3.4

**C<sub>14</sub>H<sub>23</sub>Pb**Reaction with AgNO<sub>3</sub>: 5.6.4

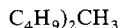
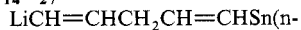
Reaction with AgX: 5.6.4.1

**C<sub>14</sub>H<sub>22</sub>S**

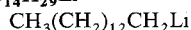
Reaction with Li metal: 5.5.2.2.5

**C<sub>14</sub>H<sub>24</sub>SSi**Reaction with a Li radical anion:  
5.5.2.2.5**C<sub>14</sub>H<sub>26</sub>ClHgNO<sub>3</sub>**

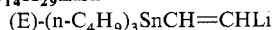
Formation: 5.7.2.3.3

**C<sub>14</sub>H<sub>27</sub>LiSn**

Formation: 5.5.2.3.1

**C<sub>14</sub>H<sub>29</sub>Li**

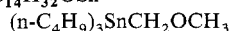
Formation: 5.5.2.2.1

**C<sub>14</sub>H<sub>29</sub>LiSn**

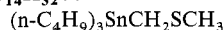
Formation: 5.5.2.3.1

**C<sub>14</sub>H<sub>30</sub>LiN**

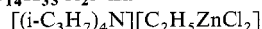
Formation: 5.5.2.3.2

**C<sub>14</sub>H<sub>32</sub>OSn**

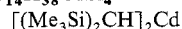
Transmetallation: 5.5.2.3.1

**C<sub>14</sub>H<sub>32</sub>SSn**

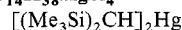
Transmetallation: 5.5.2.3.1

**C<sub>14</sub>H<sub>33</sub>Cl<sub>2</sub>NZn**

Formation: 5.7.2.2.1

**C<sub>14</sub>H<sub>38</sub>CdSi<sub>4</sub>**

Formation: 5.7.2.3.1

**C<sub>14</sub>H<sub>38</sub>HgSi<sub>4</sub>**

Formation: 5.7.2.3.1

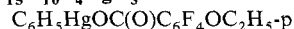
Reaction with HgX<sub>2</sub>: 5.7.2.3.2**C<sub>15</sub>H<sub>9</sub>ClFeHgMnO<sub>5</sub>**

Formation: 5.7.2.3.4

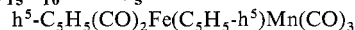
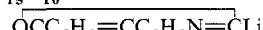
**C<sub>15</sub>H<sub>9</sub>Li**

4,5-methylenephenanthrenyllithium

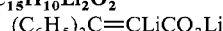
Formation: 5.5.2.2.4

**C<sub>15</sub>H<sub>10</sub>F<sub>4</sub>HgO<sub>3</sub>**

Decarboxylation: 5.7.2.3.7

**C<sub>15</sub>H<sub>10</sub>FeMnO<sub>5</sub>**Reaction with HgX<sub>2</sub>: 5.7.2.3.4**C<sub>15</sub>H<sub>10</sub>LiNO**

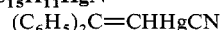
Formation: 5.5.2.3.2

**C<sub>15</sub>H<sub>10</sub>Li<sub>2</sub>O<sub>2</sub>**

Formation: 5.5.2.3.3

**C<sub>15</sub>H<sub>11</sub>Cl<sub>3</sub>FHg<sub>2</sub>O**

Formation: 5.7.2.3.4

**C<sub>15</sub>H<sub>11</sub>HgN**

Formation: 5.7.2.3.2



- C<sub>15</sub>H<sub>11</sub>KO<sub>2</sub>**  
9-carbomethoxyfluorenylpotassium  
Formation: 5.5.3.3.1
- C<sub>15</sub>H<sub>12</sub>Au<sub>3</sub>N<sub>3</sub>**  
[Au(2-C<sub>5</sub>H<sub>4</sub>N)]<sub>3</sub>  
Formation: 5.6.4.1
- C<sub>15</sub>H<sub>12</sub>ClFHgO**  
ClHgCH=C(C<sub>6</sub>H<sub>4</sub>F-p)(C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-p)  
Formation: 5.7.2.3.4
- C<sub>15</sub>H<sub>12</sub>LiN<sub>3</sub>**  
C<sub>6</sub>H<sub>5</sub>CN(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)CLiN<sup>+</sup><sub>3</sub>  
Formation: 5.5.2.3.2
- C<sub>15</sub>H<sub>13</sub>K**  
K[C<sub>6</sub>H<sub>5</sub>CH=CHCH(C<sub>6</sub>H<sub>5</sub>)]  
Formation: 5.5.3.3.2  
K[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=CHCH<sub>2</sub>]  
Formation: 5.5.3.2.6
- C<sub>15</sub>H<sub>13</sub>Li**  
C<sub>6</sub>H<sub>5</sub>CH=CHCH(Li)C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.2.4  
Substrate in metal-metal exchange:  
5.5.3.3.2  
[C<sub>6</sub>H<sub>5</sub>CH::CH::C(C<sub>6</sub>H<sub>5</sub>)H]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.3.2  
(Z)-C<sub>6</sub>H<sub>5</sub>CLi=C(C<sub>6</sub>H<sub>5</sub>)CH<sub>3</sub>  
Formation: 5.5.2.3.1
- C<sub>15</sub>H<sub>13</sub>LiO<sub>3</sub>S**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COCH(Li)SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>15</sub>H<sub>14</sub>FeO<sub>2</sub>**  
h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>15</sub>H<sub>14</sub>HgO<sub>6</sub>S<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>CHHgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.4
- C<sub>15</sub>H<sub>14</sub>Li<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>CH(Li)C(C<sub>6</sub>H<sub>5</sub>)(Li)CH<sub>3</sub>  
Formation: 5.5.2.2.3
- C<sub>15</sub>H<sub>14</sub>Li<sub>2</sub>O**  
(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)C(OLi)CH(C<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.3.5
- C<sub>15</sub>H<sub>14</sub>S<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>15</sub>H<sub>14</sub>Se<sub>2</sub>**  
1,1-(C<sub>6</sub>H<sub>5</sub>Se)<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>15</sub>H<sub>15</sub>K<sub>2</sub>**  
K<sub>2</sub>[CH(CH)<sub>6</sub>CHCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]  
Formation: 5.5.3.2.6
- C<sub>15</sub>H<sub>15</sub>Li**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>Li  
Formation: 5.5.2.2.1, 5.5.2.2.2
- C<sub>15</sub>H<sub>15</sub>LiN<sub>2</sub>**  
o-LiC<sub>6</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>)C=NN(CH<sub>3</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>15</sub>H<sub>15</sub>LiOSe**  
C<sub>6</sub>H<sub>5</sub>Se(O)CH(Li)CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>15</sub>H<sub>16</sub>LiOP**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)CH(Li)C<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>15</sub>H<sub>16</sub>S**  
C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
Reaction with C<sub>10</sub>H<sub>8</sub>K: 5.5.3.2.2  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>15</sub>H<sub>16</sub>S<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>SCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>15</sub>H<sub>16</sub>Si**  
CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>15</sub>H<sub>17</sub>BrHgN<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>NHCH<sub>2</sub>CH(NHC<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>HgBr  
Formation: 5.7.2.3.3
- C<sub>15</sub>H<sub>20</sub>Hg<sub>2</sub>O<sub>6</sub>**  
Hg<sub>2</sub>[CH<sub>3</sub>C(O)CC(O)CH<sub>3</sub>][CH<sub>3</sub>C(O)CH\*  
C(O)CH<sub>3</sub>]<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>15</sub>H<sub>20</sub>LiNO<sub>3</sub>**  
p-[O(CH<sub>2</sub>)<sub>3</sub>O(Li)C]C<sub>6</sub>H<sub>4</sub>C≡NCH<sub>2</sub>(C\*  
H<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>O  
Formation: 5.5.2.3.2
- C<sub>15</sub>H<sub>21</sub>Li**  
C<sub>6</sub>H<sub>5</sub>C(CHCH<sub>2</sub>CH<sub>2</sub>)LiCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>  
Formation: 5.5.2.3.4  
C<sub>6</sub>H<sub>5</sub>C[CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]=CHCH<sub>2</sub>CH<sub>2</sub><sup>-</sup>  
Li  
Formation: 5.5.2.3.4
- C<sub>15</sub>H<sub>24</sub>OSSi**  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH=C(SC<sub>6</sub>H<sub>5</sub>)OSi(CH<sub>3</sub>)<sub>3</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>15</sub>H<sub>25</sub>LiSSi**  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>C(Li)[Si(CH<sub>3</sub>)<sub>3</sub>]SC<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.4  
(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>C(Li)[Si(CH<sub>3</sub>)<sub>3</sub>]SC<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.4
- C<sub>15</sub>H<sub>34</sub>OSn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn(CH<sub>2</sub>)<sub>3</sub>OH  
Reaction with RLi: 5.5.2.3.1
- C<sub>15</sub>H<sub>34</sub>Sn**  
[(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>]<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Cd: 5.7.5.2.2

- Reaction with  $R_2Hg$ : 5.7.5.2.3
- C<sub>15</sub>H<sub>35</sub>LiSn<sub>2</sub>**  
 $(n-C_3H_7)_3SnSn(C_3H_7-n)_2Li$   
 Formation: 5.5.6.3.1
- C<sub>15</sub>H<sub>35</sub>NSn**  
 $(n-C_4H_9)_3SnCH_2N(CH_3)_2$   
 Transmetallation: 5.5.2.3.1
- C<sub>16</sub>F<sub>15</sub>Hg<sub>5</sub>NO<sub>12</sub>**  
 $C_6[HgOC(O)CF_3]_5NO_2$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>HF<sub>15</sub>Hg<sub>5</sub>O<sub>10</sub>**  
 $C_6[HgOC(O)CF_3]_5H$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>H<sub>6</sub>Br<sub>8</sub>HgO<sub>6</sub>**  
 $[p-CH_3OC_6Br_4C(O)O]_2Hg$   
 Decarboxylation: 5.7.2.3.7
- C<sub>16</sub>H<sub>8</sub>AgCuMnO<sub>6</sub>**  
 $[h^5-C_5H_4Mn(CO)_3]_2AgCu$   
 Formation: 5.6.4.1
- C<sub>16</sub>H<sub>10</sub>B<sub>20</sub>Zn**  
 $(C_6H_5C_2B_{10})_2Zn$   
 Formation: 5.7.2.4.1
- C<sub>16</sub>H<sub>10</sub>Cd**  
 $(C_6H_5C\equiv C)_2Cd$   
 Formation: 5.7.2.3.1
- C<sub>16</sub>H<sub>10</sub>Hg**  
 $(C_6H_5C\equiv C)_2Hg$   
 Formation: 5.7.2.3.1, 5.7.2.3.4  
 Reaction with  $Hg(CN)_2$ : 5.7.2.3.2
- C<sub>16</sub>H<sub>10</sub>HgS<sub>2</sub>**  
 $(C_6H_5SC\equiv C)_2Hg$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>H<sub>10</sub>Li<sub>2</sub>**  
 dilithiobis(cyclohepta)[cd,gh]pentalene  
 Formation: 5.5.2.2.3  
 dilithiobis(cyclohepta)[ef,kl]heptalene  
 Formation: 5.5.2.2.3  
 dilithiopyrene  
 Formation: 5.5.2.2.3
- C<sub>16</sub>H<sub>10</sub>Li<sub>4</sub>**  
 tetralithioacepleiadylene  
 Formation: 5.5.2.2.3
- C<sub>16</sub>H<sub>10</sub>Zn**  
 $(C_6H_5C\equiv C)_2Zn$   
 Formation: 5.7.2.4.1
- C<sub>16</sub>H<sub>12</sub>F<sub>10</sub>HgSi<sub>2</sub>**  
 $[C_6F_5(CH_3)_2Si]_2Hg$   
 Formation: 5.7.3.5
- C<sub>16</sub>H<sub>12</sub>HgN<sub>2</sub>**  
 $[C_6H_5CH(CN)]_2Hg$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>H<sub>12</sub>LiN**  
 $\overline{CH(C_6H_5)CH(C_6H_5)C(CN)Li}$   
 Formation: 5.5.2.3.2
- $\overline{CH_2C(C_6H_5)_2CLiNC}$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>12</sub>Li<sub>2</sub>**  
 $C_6H_5(Li)CCHCHC(Li)C_6H_5$   
 Formation: 5.5.2.3.3
- C<sub>16</sub>H<sub>12</sub>Li<sub>2</sub>O<sub>2</sub>**  
 $\overline{CH(C_6H_5)CH(C_6H_5)C(Li)CO_2Li}$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>14</sub>**  
 $C_6H_5CH=CHCH=CHC_6H_5$   
 Reaction with Li metal: 5.5.2.2.3
- C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>Hg<sub>2</sub>**  
 $(p-CH_3C_6H_4)_2C=C(HgCl)_2$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>H<sub>14</sub>HgO<sub>2</sub>**  
 $[C_6H_5C(O)CH_2]_2Hg$   
 Formation: 5.7.2.3.4, 5.7.2.3.7  
 Reaction with  $HgX_2$ : 5.7.2.3.2  
 $[p-CH_3C(O)C_6H_4]_2Hg$   
 Formation: 5.7.2.3.3
- C<sub>16</sub>H<sub>14</sub>HgO<sub>4</sub>**  
 $(m-CH_3O_2CC_6H_4)_2Hg$   
 Reaction with  $HgX_2$ : 5.7.2.3.2
- C<sub>16</sub>H<sub>14</sub>Li<sub>2</sub>**  
 $C_6H_5CH(Li)CH=CHCH(Li)C_6H_5$   
 Formation: 5.5.2.2.3
- C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>Zn**  
 $[C_6H_5C(O)OCH_2]_2Zn$   
 Formation: 5.7.2.3.5
- C<sub>16</sub>H<sub>14</sub>BrHg**  
 $(C_6H_5)_2\overline{CCH_2CCH_3}HgBr$   
 Formation: 5.7.2.3.1
- C<sub>16</sub>H<sub>15</sub>ClHgO**  
 $CH_3C(O)CH_2HgC(C_6H_5)_2Cl$   
 Formation: 5.7.2.3.3
- C<sub>16</sub>H<sub>15</sub>ClHgO<sub>2</sub>**  
 $(p-CH_3OC_6H_4)_2C=CHHgCl$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>H<sub>15</sub>Li**  
 $(C_6H_5)_2\overline{CCH_2C}(CH_3)Li$   
 Formation: 5.5.2.2.1, 5.5.2.3.3  
 Reaction with  $HgX_2$ : 5.7.2.3.1  
 $(C_6H_5)_2CLi\overline{CHCH_2CH_2}$   
 Equilibrium: 5.5.2.3.4  
 $(C_6H_5)_2C=CHCH_2CH_2Li$   
 Equilibrium: 5.5.2.3.4
- C<sub>16</sub>H<sub>15</sub>Li<sub>2</sub>O<sub>5</sub>P**  
 $(C_6H_5CH_2O)_2P(O)CH(Li)CO_2Li$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>Hg<sub>2</sub>O<sub>2</sub>**  
 $[ClHgCH_2CH(C_6H_5)O]_2$   
 Formation: 5.7.2.3.3

- C<sub>16</sub>H<sub>16</sub>LiOP**  
 $[\text{CH}_3\text{CH}=\text{CH}=\text{CHP}(\text{O})(\text{C}_6\text{H}_5)_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>16</sub>Li<sub>2</sub>**  
 $[\text{CH}(\text{CH})_{14}\text{CH}]^{2-} 2\text{Li}^+$   
 Formation: 5.5.2.2.3  
 $\text{CH}_3\text{CH}(\text{C}_6\text{H}_4\text{CH}_2\text{Li-p})_2$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>16</sub>S<sub>2</sub>**  
 $(\text{CH}_3)_2\text{C}=\text{C}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion:  
 5.5.2.2.5  
 $(\text{C}_6\text{H}_5\text{S})_2\text{CCH}(\text{CH}_3)_2\text{CH}_2$   
 Reaction with a Li radical anion:  
 5.5.2.2.5
- C<sub>16</sub>H<sub>16</sub>Se<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{Se})_2\text{C}(\text{CH}_2)_2\text{CH}_2$   
 Transmetallation: 5.5.2.3.1
- C<sub>16</sub>H<sub>17</sub>Li**  
 $\text{CH}_3\text{CH}(\text{C}_6\text{H}_4\text{CH}_3\text{-p})(\text{C}_6\text{H}_4\text{CH}_2\text{Li-p})$   
 Formation: 5.5.2.3.2  
 $\text{LiC}(\text{CH}_3)(\text{C}_6\text{H}_4\text{CH}_3\text{-p})_2$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>18</sub>AsLi**  
 $(\text{C}_6\text{H}_5)_2\text{AsCH}(\text{Li})\text{CH}_2\text{CH}_2\text{CH}_3$   
 Formation: 5.5.2.3.4
- C<sub>16</sub>H<sub>18</sub>Hg**  
 $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2)_2\text{Hg}$   
 Formation: 5.7.2.3.1
- C<sub>16</sub>H<sub>18</sub>LiNO<sub>2</sub>S**  
 $\text{C}_6\text{H}_5\text{CH}[\text{N}(\text{CH}_3)_2]\text{CH}(\text{Li})\text{SO}_2\text{C}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>18</sub>OS**  
 $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.5
- C<sub>16</sub>H<sub>18</sub>S**  
 $\text{p}-(\text{CH}_3\text{CH}_2)\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SC}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.5
- C<sub>16</sub>H<sub>18</sub>S<sub>2</sub>**  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion:  
 5.5.2.2.5  
 $(\text{CH}_3)_2\text{CHCH}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion:  
 5.5.2.2.5
- C<sub>16</sub>H<sub>18</sub>Zn**  
 $(\text{C}_6\text{H}_5\text{CHCH}_3)_2\text{Zn}$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1  
 $\text{Zn}[\text{C}_6\text{H}_3(\text{CH}_3)_2\text{-2,6}]_2$   
 Reaction with CuX, AgX, AuX<sub>3</sub>: 5.6.4.1
- C<sub>16</sub>H<sub>19</sub>ClSi**  
 $(\text{CH}_3)_3\text{C}(\text{C}_6\text{H}_5)_2\text{SiCl}$   
 Reaction with Li metal: 5.5.4.3
- C<sub>16</sub>H<sub>19</sub>LiSi**  
 $(\text{CH}_3)_3\text{C}(\text{C}_6\text{H}_5)_2\text{SiLi}$   
 Formation: 5.5.4.3
- C<sub>16</sub>H<sub>19</sub>LiSn**  
 $\text{CH}_3(\text{C}_6\text{H}_5)\text{CHCH}_2(\text{CH}_3)\text{C}_6\text{H}_5\text{SnLi}$   
 Formation: 5.5.6.3.1
- C<sub>16</sub>H<sub>20</sub>HgN<sub>2</sub>**  
 $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{Hg}$   
 Reaction with Zn metal: 5.7.2.2.2
- C<sub>16</sub>H<sub>20</sub>LiSSi**  
 $\text{C}_6\text{H}_5\text{SCH}(\text{Li})\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.2
- C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>Zn**  
 $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_2\text{Zn}$   
 Formation: 5.7.2.2.2
- C<sub>16</sub>H<sub>20</sub>Pb**  
 $(\text{C}_6\text{H}_5)_2\text{Pb}(\text{C}_2\text{H}_5)_2$   
 Formation: 5.5.7.4
- C<sub>16</sub>H<sub>20</sub>SSI**  
 $(\text{CH}_3)_2\text{SiCH}(\text{C}_6\text{H}_5)\text{SC}_6\text{H}_5$   
 Reaction with a Li radical anion:  
 5.5.2.2.5
- C<sub>16</sub>H<sub>20</sub>Si<sub>2</sub>**  
 $\text{C}_6\text{H}_5(\text{CH}_3)\text{SiCH}_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{CH}_2$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>16</sub>H<sub>22</sub>HgSi<sub>2</sub>**  
 $[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{Si}]_2\text{Hg}$   
 Reaction with Mg metal: 5.7.3.1
- C<sub>16</sub>H<sub>22</sub>Si<sub>2</sub>**  
 $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{SiSiC}_6\text{H}_5(\text{CH}_3)_2$   
 Reaction with Na metal: 5.5.4.2.1
- C<sub>16</sub>H<sub>23</sub>LiS<sub>2</sub>**  
 $(\text{H}_3\text{C})_3\text{CCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}(\text{Li})\text{S}(\text{CH}_2)_3\text{S}$   
 Formation: 5.5.2.3.4
- C<sub>16</sub>H<sub>24</sub>HgO<sub>2</sub>**  
 $2,6-[(\text{CH}_3)_3\text{C}]_2\text{-4-H}_3\text{CC}(\text{O})\text{HgC}_6\text{H}_2\text{OH}$   
 Formation: 5.7.2.3.4
- C<sub>16</sub>H<sub>27</sub>BO<sub>2</sub>**  
 $(\text{R})(-)\text{C}_6\text{H}_5\text{C}(\text{CH}_3)\text{HB}(\text{OC}_4\text{H}_9\text{-n})_2$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.7
- C<sub>16</sub>H<sub>28</sub>Sn**  
 $(\text{CH}_3\text{CH}=\text{CHCH}_2)_4\text{Sn}$   
 Transmetallation: 5.5.2.3.1
- C<sub>16</sub>H<sub>33</sub>Li**  
 $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>16</sub>H<sub>34</sub>Hg**  
 $[(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{H}]_2\text{Hg}$   
 Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>16</sub>H<sub>34</sub>Zn**  
 $(\text{C}_8\text{H}_{17})_2\text{Zn}$   
 Formation: 5.7.2.3.1

- C<sub>16</sub>H<sub>36</sub>Ge**  
 $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{Ge}$   
 Reaction with Li metal: 5.5.5.5
- C<sub>16</sub>H<sub>36</sub>HgSn**  
 $t\text{-C}_4\text{H}_9\text{HgSn}(\text{C}_4\text{H}_9\text{-}i)_3$   
 Formation: 5.7.5.4
- C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Sn**  
 $(i\text{-C}_3\text{H}_7\text{OCH}_2)_4\text{Sn}$   
 Transmetallation: 5.5.2.3.1
- C<sub>16</sub>H<sub>37</sub>NOSn**  
 $(n\text{-C}_4\text{H}_9)_3\text{SnCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$   
 Transmetallation: 5.5.2.3.1
- C<sub>16</sub>H<sub>38</sub>SiSn**  
 $(n\text{-C}_4\text{H}_9)_3\text{SnCH}_2\text{Si}(\text{CH}_3)_3$   
 Reaction with RLi: 5.5.2.3.1  
 Transmetallation: 5.5.2.3.1
- C<sub>16</sub>H<sub>40</sub>HgSi<sub>3</sub>**  
 $(\text{C}_2\text{H}_5)_3\text{SiHgSi}(\text{C}_2\text{H}_5)_2\text{Si}(\text{C}_2\text{H}_5)_3$   
 Formation: 5.7.3.3  
 Reaction with K metal: 5.5.4.6
- C<sub>16</sub>H<sub>44</sub>Cu<sub>4</sub>Si<sub>4</sub>**  
 $[\text{CuCH}_2\text{Si}(\text{CH}_3)_3]_4$   
 Formation: 5.6.4
- C<sub>16</sub>H<sub>44</sub>Si<sub>4</sub>Sn**  
 $[(\text{CH}_3)_3\text{SiCH}_2]_4\text{Sn}$   
 Formation: 5.7.5.2.3
- C<sub>17</sub>H<sub>3</sub>F<sub>15</sub>Hg<sub>5</sub>O<sub>10</sub>**  
 $\text{CH}_3\text{C}_6[\text{HgOC}(\text{O})\text{CF}_3]_5$   
 Formation: 5.7.2.3.4
- C<sub>17</sub>H<sub>14</sub>Li<sub>2</sub>O<sub>2</sub>S**  
 $(\text{C}_6\text{H}_5)_2\overline{\text{CS}(\text{O})_2\text{C}(\text{Li})_2\text{CH}=\text{CHCH}_2}$   
 Formation: 5.5.2.3.2
- C<sub>17</sub>H<sub>15</sub>Li**  
 $[\text{CH}_2\text{CH}_2\text{CH}\cdots\text{C}\cdots\text{C}(\text{C}_6\text{H}_5)_2]^- \text{Li}^+$   
 Formation: 5.5.2.3.2  
 $\text{CH}_3\text{C}\equiv\text{CC}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- C<sub>17</sub>H<sub>16</sub>Ge**  
 $\text{CH}_3(\text{C}_6\text{H}_5)(1\text{-C}_{10}\text{H}_7)\text{GeH}$   
 Reaction with RLi: 5.5.5.4  
 Reaction with R<sub>2</sub>Hg: 5.7.4.2
- C<sub>17</sub>H<sub>16</sub>HgO<sub>4</sub>**  
 $\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}(\text{C}_6\text{H}_5)(\text{OCH}_3)\text{HgOC}(\text{O})\text{CH}_3$   
 Formation: 5.7.2.3.3
- C<sub>17</sub>H<sub>16</sub>Hg<sub>2</sub>O<sub>8</sub>S<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{SO}_2)_2\text{C}[\text{HgOC}(\text{O})\text{CH}_3]_2$   
 Formation: 5.7.2.3.4
- C<sub>17</sub>H<sub>16</sub>Si**  
 $\text{CH}_3(\text{C}_6\text{H}_5)(1\text{-C}_{10}\text{H}_7)\text{SiH}$   
 Reaction with R<sub>2</sub>Hg: 5.7.3.3
- C<sub>17</sub>H<sub>17</sub>Li**  
 $[\text{CH}\cdots(\text{CH})_{15}\cdots\text{CH}]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>17</sub>H<sub>17</sub>LiSi**  
 $[\text{CH}_2=\text{CHSi}(\text{C}_6\text{H}_5)_2\text{CH}\cdots\text{CH}\cdots\text{CH}_2]^* \text{Li}^+$   
 Formation: 5.5.2.3.4
- C<sub>17</sub>H<sub>18</sub>LiN**  
 $(\text{Z})\text{-o-}(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CLi}=\text{C}(\text{C}_6\text{H}_5)\text{CH}_3$   
 Formation: 5.5.2.3.1
- C<sub>17</sub>H<sub>18</sub>S<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{S})_2\overline{\text{CC}(\text{CH}_3)_2\text{CH}_2}$   
 Reaction with a Li radical anion: 5.5.2.2.5
- C<sub>17</sub>H<sub>19</sub>Li**  
 $(\text{C}_6\text{H}_5)_2\text{C}(\text{Li})\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$   
 Formation: 5.5.2.3.5
- C<sub>17</sub>H<sub>19</sub>LiNO<sub>2</sub>P**  
 $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{Li})(\text{CH}_2)_2\text{OCH}_2\text{CH}_2$   
 Formation: 5.5.2.3.2
- C<sub>17</sub>H<sub>20</sub>SSn**  
 $(\text{CH}_3)_3\text{SnC}[\text{S}(\text{C}_6\text{H}_5)]_2=\text{CH}(\text{C}_6\text{H}_5)$   
 Transmetallation: 5.5.2.3.1
- C<sub>17</sub>H<sub>20</sub>S<sub>2</sub>**  
 $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion: 5.5.2.2.5  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion: 5.5.2.2.5
- C<sub>17</sub>H<sub>25</sub>LiO<sub>2</sub>**  
 $2,4,6\text{-}(i\text{-C}_3\text{H}_7)_3\text{C}_6\text{H}_2\text{CO}_2\text{CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- C<sub>17</sub>H<sub>27</sub>Li**  
 $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{CH}(n\text{-C}_4\text{H}_9)\text{CH}_2(\text{CH}_2)_3\text{CH}_3$   
 Formation: 5.5.2.3.4
- C<sub>17</sub>H<sub>27</sub>LiOSe**  
 $2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2\text{SeOCH}(\text{Li})\text{C}_7\text{H}_{15}$   
 Formation: 5.5.2.3.2
- C<sub>17</sub>H<sub>31</sub>B**  
 $(\text{E})\text{-}(\text{C}_3\text{H}_7\text{CH}=\text{CH})\text{B}(\text{cyclo-C}_6\text{H}_{11})_2$   
 Formation: 5.7.2.3.1  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>17</sub>H<sub>31</sub>Li**  
 $\text{CH}_3(\text{CH}_2)_{14}\text{C}\equiv\text{CLi}$   
 Formation: 5.5.2.2.2
- C<sub>17</sub>H<sub>36</sub>OSSn**  
 $(\text{E})\text{-(n-C}_4\text{H}_9)_3\text{SnCH}=\text{CHCH}_2\text{OCH}_2\text{CH}_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>17</sub>H<sub>38</sub>AgClP<sub>2</sub>Si<sub>2</sub>**  
 $[\text{Ag}[\text{CHSiMe}_3=\text{PMe}_3]_2]\text{Cl}$   
 Formation: 5.6.4.3
- C<sub>17</sub>H<sub>38</sub>Li<sub>2</sub>OSn**  
 $[(n\text{-C}_4\text{H}_9)_4\overline{\text{SnCH}_2\text{O}}]\text{Li}_2$   
 Formation: 5.5.2.3.1

- C<sub>17</sub>H<sub>38</sub>O<sub>2</sub>Sn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH<sub>2</sub>OCH(CH<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>17</sub>H<sub>38</sub>SiSn**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiCH=CHSn(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>18</sub>BrF<sub>15</sub>Ge**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeBr  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.6
- C<sub>18</sub>BrF<sub>15</sub>Sn**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>SnBr  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.5.3
- C<sub>18</sub>ClF<sub>15</sub>Ge**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeCl  
Formation: 5.7.4.5  
Reaction with Li metal: 5.5.5.3
- C<sub>18</sub>F<sub>15</sub>GeLi**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeLi  
Formation: 5.5.5.3
- C<sub>18</sub>F<sub>15</sub>PbLi**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>PbLi  
Formation: 5.5.7.5
- C<sub>18</sub>F<sub>18</sub>Hg<sub>6</sub>O<sub>12</sub>**  
C<sub>6</sub>[HgOC(O)CF<sub>3</sub>]<sub>6</sub>  
Formation: 5.7.2.3.4
- C<sub>18</sub>HF<sub>15</sub>Ge**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeH  
Reaction with R<sub>2</sub>Zn, R<sub>2</sub>Cd or R<sub>2</sub>Hg:  
5.7.4.2  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.2  
Reaction with [(R<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Hg: 5.7.4.2
- C<sub>18</sub>HF<sub>15</sub>Sn**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Cd: 5.7.5.2.2  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3
- C<sub>18</sub>H<sub>2</sub>Cl<sub>12</sub>Hg<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**  
o-(o-HC<sub>6</sub>Cl<sub>4</sub>SO<sub>3</sub>Hg)<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>  
Formation: 5.7.2.3.7
- C<sub>18</sub>H<sub>2</sub>F<sub>12</sub>Hg<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**  
p-(p-HC<sub>6</sub>F<sub>4</sub>SO<sub>3</sub>Hg)<sub>2</sub>C<sub>6</sub>F<sub>4</sub>  
Formation: 5.7.2.3.7
- C<sub>18</sub>H<sub>10</sub>ClF<sub>5</sub>Si**  
C<sub>6</sub>F<sub>5</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl  
Reaction with Li metal: 5.5.4.2.2, 5.5.4.3
- C<sub>18</sub>H<sub>10</sub>Cr<sub>2</sub>HgO<sub>6</sub>**  
[(CO)<sub>3</sub>CrC<sub>6</sub>H<sub>5</sub>-h<sup>6</sup>]<sub>2</sub>Hg  
Transmetallation: 5.5.2.3.1
- C<sub>18</sub>H<sub>12</sub>BiCl<sub>3</sub>**  
(p-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Bi  
Transmetallation: 5.5.2.3.1
- C<sub>18</sub>H<sub>12</sub>Br<sub>3</sub>Sb**  
(p-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb  
Transmetallation: 5.5.2.3.1
- C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>Sb**  
(p-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb  
Transmetallation: 5.5.2.3.1
- C<sub>18</sub>H<sub>12</sub>Li<sub>2</sub>**  
2,2'-o-LiC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.2
- C<sub>18</sub>H<sub>13</sub>CuN<sub>2</sub>**  
CuC≡CPh[CH(CH<sub>3</sub>)<sub>3</sub>NCCN(CH<sub>3</sub>)<sub>3</sub>CH]  
Formation: 5.6.4.3
- C<sub>18</sub>H<sub>14</sub>HgO<sub>2</sub>**  
cis-[C<sub>6</sub>H<sub>5</sub>C(O)CH=CH]<sub>2</sub>Hg  
Reaction with HgX<sub>2</sub>: 5.7.2.3.2
- C<sub>18</sub>H<sub>14</sub>K<sub>2</sub>**  
[C<sub>18</sub>H<sub>14</sub>]<sup>2-</sup> 2K<sup>+</sup>  
Formation: 5.5.3.2.4
- C<sub>18</sub>H<sub>14</sub>K<sub>4</sub>**  
[C<sub>18</sub>H<sub>14</sub>]<sup>4-</sup> 4K<sup>+</sup>  
Formation: 5.5.3.2.4
- C<sub>18</sub>H<sub>14</sub>Li<sub>2</sub>**  
dilithio-1,9-dimethyldibenzo[b,f]pentalene  
Formation: 5.5.2.2.3
- C<sub>18</sub>H<sub>15</sub>As**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>As  
Reaction with Li metal: 5.5.2.2.5
- C<sub>18</sub>H<sub>15</sub>AuClP**  
AuCl · PPh<sub>3</sub>  
Reaction with R<sub>3</sub>GeLi: 5.6.5.1  
Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.6.5.3  
Reaction with RLi: 5.6.4  
Reaction with R<sub>3</sub>SiLi: 5.6.5.1  
Reaction with TiR<sub>2</sub>Cl: 5.6.4.1
- C<sub>18</sub>H<sub>15</sub>AuCl<sub>3</sub>PSn**  
Cl<sub>3</sub>Sn · PPh<sub>3</sub>  
Formation: 5.6.5.4
- C<sub>18</sub>H<sub>15</sub>BrCuP**  
CuBr · PPh<sub>3</sub>  
Reaction with TiR: 5.6.4.1
- C<sub>18</sub>H<sub>15</sub>BrGe**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeBr  
Reaction with Li metal: 5.5.5.3
- C<sub>18</sub>H<sub>15</sub>BrSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnBr  
Reaction with Na metal: 5.5.6.3.2
- C<sub>18</sub>H<sub>15</sub>CdClSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCdCl  
Formation: 5.7.5  
Formation of complexes: 5.7.5.1.2, 5.7.5.2.2
- C<sub>18</sub>H<sub>15</sub>CdLi**  
Li[Cd(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]  
Formation: 5.7.2.4.3
- C<sub>18</sub>H<sub>15</sub>ClGe**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeCl  
Formation: 5.6.5.4

- Reaction with Li metal: 5.5.5.3
- C<sub>18</sub>H<sub>15</sub>ClHgPb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbHgCl  
Decomposition: 5.7.6.2
- C<sub>18</sub>H<sub>15</sub>ClHgSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnHgCl  
Formation: 5.7.5  
Formation of Bipy complex: 5.7.5.1.3
- C<sub>18</sub>H<sub>15</sub>ClPb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCl  
Reaction with Li metal: 5.5.7.4
- C<sub>18</sub>H<sub>15</sub>ClSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiCl  
Reaction with Na-Hg: 5.7.3.2  
Reaction with Li, Na, K, Rb or Cs metal: 5.5.4.3  
Reaction with Na, Cs, Li, Na-K or Rb metal: 5.5.4.2.2
- C<sub>18</sub>H<sub>15</sub>ClSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCl  
Formation: 5.7.5.1.1  
Reaction with Cd metal: 5.7.5.1.2  
Reaction with Hg metal: 5.7.5.1.3  
Reaction with Zn-Cu couple: 5.7.5.1.1  
Reaction with Na metal: 5.5.6.3.2
- C<sub>18</sub>H<sub>15</sub>ClSnZn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn · C<sub>6</sub>H<sub>5</sub>ZnCl  
Formation: 5.7.5.1.1  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnZnCl  
Formation: 5.7.5, 5.7.5.1.1, 5.7.5.2.1  
Formation of complex: 5.7.5.2.1
- C<sub>18</sub>H<sub>15</sub>CsSi**  
Cs[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.2.1, 5.5.4.2.2, 5.5.4.3
- C<sub>18</sub>H<sub>15</sub>FGe**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeF  
Formation: 5.7.4.8
- C<sub>18</sub>H<sub>15</sub>FSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiF  
Reaction with Li metal: 5.5.4.3, 5.5.4.2.2
- C<sub>18</sub>H<sub>15</sub>GeK**  
K[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]  
Formation: 5.5.5.2.1, 5.5.5.4, 5.5.5.5
- C<sub>18</sub>H<sub>15</sub>GeLi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeLi  
Formation: 5.5.5.2.1, 5.5.5.2.2, 5.5.5.3, 5.5.5.4, 5.5.5.5, 5.5.5.6, 5.6.5.1  
Reaction with GeI<sub>2</sub>: 5.5.5.7
- C<sub>18</sub>H<sub>15</sub>GeNa**  
Na[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]  
Formation: 5.5.5.2.1, 5.5.5.2.2, 5.5.5.4  
Reaction with ZnX<sub>2</sub>: 5.7.4.1
- C<sub>18</sub>H<sub>15</sub>KPb**  
K[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.2.1
- C<sub>18</sub>H<sub>15</sub>KSi**  
K[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.2.1, 5.5.4.2.2, 5.5.4.3, 5.5.4.5, 5.5.4.4, 5.7.3.1  
Reaction with ZnX<sub>2</sub>: 5.7.3.1
- C<sub>18</sub>H<sub>15</sub>KSn**  
K[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]  
Reaction with ZnX<sub>2</sub>: 5.7.5  
K[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6
- C<sub>18</sub>H<sub>15</sub>LiPb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbLi  
Formation: 5.5.7.2.1, 5.5.7.2.2, 5.5.7.4, 5.5.7.5, 5.5.7.6  
Reaction with HgX<sub>2</sub>: 5.7.6.2
- C<sub>18</sub>H<sub>15</sub>LiSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiLi  
Formation: 5.5.4.2.1, 5.5.4.2.2, 5.5.4.3, 5.5.4.5, 5.5.4.7  
Reaction with (Ph<sub>2</sub>Si)<sub>5</sub>: 5.5.4.2.2  
Reaction with ArHgX: 5.7.3.1  
Reaction with CuX: 5.6.5.1  
Reaction with AuX: 5.6.5.1
- C<sub>18</sub>H<sub>15</sub>LiSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnLi  
Formation: 5.5.6.2.1  
Reaction with R<sub>3</sub>SiCl: 5.5.4.7  
Reaction with SnCl<sub>2</sub>: 5.5.6.6
- C<sub>18</sub>H<sub>15</sub>LiZn**  
Li[Zn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]  
Formation and structure: 5.7.2.4.3
- C<sub>18</sub>H<sub>15</sub>N**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>N  
Reaction with Li metal: 5.5.2.2.5
- C<sub>18</sub>H<sub>15</sub>NaPb**  
Na[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.4, 5.5.7.2.1, 5.5.7.3
- C<sub>18</sub>H<sub>15</sub>NaSi**  
Na[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.2.2  
Formation from disilane: 5.5.4.2.1
- C<sub>18</sub>H<sub>15</sub>NaSn**  
Na[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]  
Formation: 5.5.6.2.2, 5.5.6.3.2, 5.5.6.5  
Reaction with RBr: 5.5.6.5
- C<sub>18</sub>H<sub>15</sub>P**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P  
Reaction with Li metal: 5.5.2.2.5
- C<sub>18</sub>H<sub>15</sub>PbRb**  
Rb[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.2.1

- C<sub>18</sub>H<sub>15</sub>RbSi**  
Rb[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.2.1, 5.5.4.2.2, 5.5.4.3
- C<sub>18</sub>H<sub>15</sub>Sb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb  
Reaction with Li metal: 5.5.2.2.5
- C<sub>18</sub>H<sub>16</sub>Ge**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeH  
Deprotonation by RLi: 5.5.5.4  
Reaction with BuLi, PhLi, MeLi: 5.5.5.4  
Reaction with Dimsyl Na: 5.5.5.4  
Reaction with NaH, KH: 5.5.5.4  
Reaction with Na metal: 5.5.5.4, 5.5.5.4  
Reaction with R<sub>2</sub>Zn: 5.7.4.2
- C<sub>18</sub>H<sub>16</sub>Li<sub>2</sub>**  
dilithio-15,16-dimethyl-15,16-dihydropyr-  
ene  
Formation: 5.5.2.2.3
- C<sub>18</sub>H<sub>16</sub>Si**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiH  
Reaction with R<sub>2</sub>Hg: 5.7.3.3  
Reaction with Na-K: 5.5.4.4  
Reaction with NaH or KH: 5.5.4.4
- C<sub>18</sub>H<sub>16</sub>Sn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnH  
Reaction with KH: 5.5.6  
Reaction with RCDCl: 5.7.5.2.2  
Reaction with R<sub>2</sub>Cd: 5.7.5.2.2  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3  
Reaction with [(R<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Hg: 5.7.5  
Reaction with RLi: 5.5.6  
Reaction with RZnCl: 5.7.5.2.1  
Reaction with R<sub>2</sub>Zn: 5.7.5.2.1
- C<sub>18</sub>H<sub>17</sub>NSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiNH<sub>2</sub>  
Formation: 5.7.3.2
- C<sub>18</sub>H<sub>18</sub>Ge**  
C<sub>2</sub>H<sub>5</sub>(1-C<sub>10</sub>H<sub>7</sub>)(C<sub>6</sub>H<sub>5</sub>)GeH  
Reaction with RLi: 5.5.5.4
- C<sub>18</sub>H<sub>18</sub>HgO<sub>2</sub>**  
(C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>-o)<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>18</sub>H<sub>18</sub>Li<sub>2</sub>**  
o-LiC<sub>6</sub>H<sub>4</sub>C(n-C<sub>4</sub>H<sub>9</sub>)=C(C<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.3.4
- C<sub>18</sub>H<sub>18</sub>Li<sub>2</sub>Si**  
C<sub>6</sub>H<sub>5</sub> $\overline{\text{C}}(\text{Li})\text{CH}=\text{CHC}(\text{Li})[\text{Si}(\text{CH}_3)_2]\text{C}_6\text{H}_5$   
Formation: 5.5.2.2.3
- C<sub>18</sub>H<sub>18</sub>Si**  
C<sub>6</sub>H<sub>5</sub> $\overline{\text{C}}=\text{CHCH}=\text{C}[\text{Si}(\text{CH}_3)_2]\text{C}_6\text{H}_5$   
Reaction with Li metal: 5.5.2.2.3
- C<sub>18</sub>H<sub>19</sub>K**  
K[C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)=CC<sub>6</sub>H<sub>5</sub>]  
Formation: 5.5.3.3.3
- C<sub>18</sub>H<sub>20</sub>AuP**  
C<sub>6</sub>H<sub>5</sub>Au·PPh<sub>3</sub>  
Reaction with TiR<sub>2</sub>Br: 5.6.4.1
- C<sub>18</sub>H<sub>20</sub>Cu<sub>2</sub>N<sub>2</sub>**  
[CuC(=NCH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-2]<sub>2</sub>  
Formation: 5.6.4.4
- C<sub>18</sub>H<sub>20</sub>HgO<sub>3</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(OCH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>HgOC(O)CH<sub>3</sub>  
Formation: 5.7.2.3.3
- C<sub>18</sub>H<sub>20</sub>Li<sub>2</sub>**  
LiCH(C<sub>6</sub>H<sub>5</sub>)(CH<sub>2</sub>)<sub>4</sub>CH(C<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.2.5
- C<sub>18</sub>H<sub>20</sub>Na<sub>2</sub>**  
Na[CH<sub>3</sub>CPhCH<sub>2</sub>CH<sub>2</sub>PhCCH<sub>3</sub>]<sub>2</sub>Na  
Base for metallation reaction: 5.5.3.3.1
- C<sub>18</sub>H<sub>21</sub>Cl**  
p-(C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>Cl  
Reaction with Na, K or Cs: 5.5.3.2.1
- C<sub>18</sub>H<sub>21</sub>Cs**  
[p-(C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Cs  
Formation: 5.5.3.2.1
- C<sub>18</sub>H<sub>21</sub>Li**  
H(n-C<sub>4</sub>H<sub>9</sub>) $\overline{\text{C}}(\text{CH}_3)_5\text{C}[\text{CH}(\text{C}_6\text{H}_5)\text{Li}]$   
Formation: 5.5.2.3.4
- C<sub>18</sub>H<sub>22</sub>AsLi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>AsCH(Li)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.4  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>AsCH(Li)(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>18</sub>H<sub>22</sub>LiP**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH(Li)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.2.3.4  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH(Li)(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>18</sub>H<sub>22</sub>OS<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>  
H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>18</sub>H<sub>22</sub>S<sub>2</sub>**  
CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with a Li radical anion:  
5.5.2.2.5
- C<sub>18</sub>H<sub>24</sub>Au<sub>2</sub>N<sub>2</sub>**  
[Au(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)]<sub>2</sub>  
Formation: 5.6.4
- C<sub>18</sub>H<sub>24</sub>CuLiN<sub>2</sub>**  
CuLi(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)<sub>2</sub>  
Formation: 5.6.4
- C<sub>18</sub>H<sub>24</sub>GeN<sub>3</sub>Na**  
Na[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]·3 NH<sub>3</sub>  
Formation: 5.5.5, 5.5.5.2.1
- C<sub>18</sub>H<sub>24</sub>HgN<sub>2</sub>**  
[o-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.1

- Reaction with  $\text{HgX}_2$ : 5.7.2.3.2  
 Reaction with Zn metal: 5.7.2.2.2
- $\text{C}_{18}\text{H}_{24}\text{N}_2\text{Zn}$**   
 $[\text{o}-(\text{CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4]_2\text{Zn}$   
 Formation: 5.7.2.2.2, 5.7.2.3.1
- $\text{C}_{18}\text{H}_{25}\text{CrLiO}_4\text{Si}$**   
 $\text{h}^6\text{-(i-C}_3\text{H}_7)_3\text{SiOC}_6\text{H}_4\text{Li-m]Cr(CO)}_3$   
 Formation: 5.5.2.3.2
- $\text{C}_{18}\text{H}_{26}\text{Hg}$**   
 $[(\text{CH}_3)_3\text{CC}_5\text{H}_4]_2\text{Hg}$   
 Formation: 5.7.2.3.1
- $\text{C}_{18}\text{H}_{27}\text{LiOS}$**   
 $2,4,6\text{-(i-C}_3\text{H}_7)_3\text{C}_6\text{H}_2\text{C(O)SCH(CH}_3\text{)Li}$   
 Formation: 5.5.2.3.2
- $\text{C}_{18}\text{H}_{27}\text{LiO}_2$**   
 $2,4,6\text{-(i-C}_3\text{H}_7)_3\text{C}_6\text{H}_2\text{C(O)OCH(CH}_3\text{)Li}$   
 Formation: 5.5.2.3.1
- $\text{C}_{18}\text{H}_{28}\text{LiNO}$**   
 $2,4,6\text{-(i-C}_3\text{H}_7)_3\text{C}_6\text{H}_2\text{CON(CH}_3\text{)CH}_2\text{Li}$   
 Formation: 5.5.2.3.2
- $\text{C}_{18}\text{H}_{28}\text{Si}_3$**   
 $[(\text{CH}_3)_3\text{Si}]_2\text{Si(C}_6\text{H}_5)_2$   
 Reaction with Li metal: 5.5.4.5
- $\text{C}_{18}\text{H}_{29}\text{Li}$**   
 $\text{p-}[\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2]\text{C}_6\text{H}_4\text{Li}$   
 Formation: 5.5.2.2.1  
 $2,4,6\text{-(CH}_3)_3\text{C}_3\text{C}_6\text{H}_2\text{Li}$   
 Formation: 5.5.2.3.3
- $\text{C}_{18}\text{H}_{33}\text{B}$**   
 $(\text{cyclo-C}_6\text{H}_{11})_3\text{B}$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{Hg}_2(\text{OR})_2$ : 5.7.2.3.1  
 $(\text{Z})\text{-C}_2\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{B}(\text{cyclo-C}_6\text{H}_{11})_2$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- $\text{C}_{18}\text{H}_{33}\text{Cl}_2\text{NZn}$**   
 $[(\text{i-C}_3\text{H}_7)_4\text{N}][\text{C}_6\text{H}_5\text{ZnCl}_2]$   
 Formation: 5.7.2.2.1
- $\text{C}_{18}\text{H}_{33}\text{LiSi}_2$**   
 $[(\text{CH}_3)_3\text{Si}]_2\text{C(Li)C(C}_6\text{H}_5\text{)HC(CH}_3\text{)}_3$   
 Formation: 5.5.2.3.4
- $\text{C}_{18}\text{H}_{33}\text{NaPb}$**   
 $\text{Na}[(\text{C}_6\text{H}_{11})_3\text{Pb}]$   
 Formation: 5.5.7.4, 5.5.7.2.1, 5.5.7.3
- $\text{C}_{18}\text{H}_{33}\text{NaSn}$**   
 $\text{Na}[(\text{cyclo-C}_6\text{H}_{11})_3\text{Sn}]$   
 Formation: 5.5.6.2.2
- $\text{C}_{18}\text{H}_{34}\text{B}$**   
 $(\text{E})\text{-(CH}_3)_3\text{CCH}=\text{CHB}(\text{cyclo-C}_6\text{H}_{11})_2$   
 Formation: 5.7.2.3.1  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- $\text{C}_{18}\text{H}_{35}\text{B}$**   
 $\text{n-C}_6\text{H}_{13}\text{B}(\text{cyclo-C}_6\text{H}_{11})_2$   
 Formation: 5.7.2.3.1
- Reaction with  $\text{HgX}_2$ : 5.7.2.3.1
- $\text{C}_{18}\text{H}_{36}\text{OSn}$**   
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}=\text{CHCH}=\text{CHOC}_2\text{H}_5$   
 Transmetalation: 5.5.2.3.1
- $\text{C}_{18}\text{H}_{37}\text{Li}$**   
 $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{Li}$   
 Formation: 5.5.2.2.1
- $\text{C}_{18}\text{H}_{39}\text{NSn}$**   
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}_2(\text{CH}_2)_4\text{CH}_2$   
 Transmetalation: 5.5.2.3.1
- $\text{C}_{18}\text{H}_{40}\text{O}_2\text{Sn}$**   
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Transmetalation: 5.5.2.3.1
- $\text{C}_{18}\text{H}_{42}\text{Ge}_2$**   
 $(\text{i-C}_3\text{H}_7)_3\text{GeGe}(\text{i-C}_3\text{H}_7)_3$   
 Reaction with Li metal: 5.5.5.2.1
- $\text{C}_{18}\text{H}_{42}\text{Ge}_2\text{Hg}$**   
 $[(\text{i-C}_3\text{H}_7)_3\text{Ge}]_2\text{Hg}$   
 Reaction with Li metal: 5.5.5.6
- $\text{C}_{18}\text{H}_{42}\text{HgSn}_2$**   
 $[(\text{C}_3\text{H}_7)_3\text{Sn}]_2\text{Hg}$   
 Formation: 5.7.5.2.3
- $\text{C}_{18}\text{H}_{45}\text{Ge}_3\text{Ti}$**   
 $[(\text{C}_2\text{H}_5)_3\text{Ge}]_3\text{Ti}$   
 Reaction with Li metal: 5.5.5.6
- $\text{C}_{18}\text{H}_{54}\text{Si}_8$**   
 $[(\text{CH}_3)_3\text{Si}]_3\text{SiSi}[\text{Si}(\text{CH}_3)_3]_3$   
 Reaction with Li metal: 5.5.4.2.1  
 Reaction with  $\text{RLi}$ : 5.5.4.2.2
- $\text{C}_{18}\text{Li}$**   
 $\text{LiC}_{18}$   
 Formation: 5.5.2.1
- $\text{C}_{19}\text{H}_{13}\text{K}$**   
 $\text{K}[\text{C}(\text{CH})_4\text{CC}(\text{CH})_4\text{CC(Ph)}]$   
 Formation: 5.5.3.2.6
- $\text{C}_{19}\text{H}_{13}\text{Li}$**   
 9-Lithio-9-phenylfluorene  
 Formation: 5.5.2.2.5  
 9-phenylfluorenyllithium  
 Formation: 5.5.2.2.4
- $\text{C}_{19}\text{H}_{15}\text{Cl}$**   
 $(\text{C}_6\text{H}_5)_3\text{CCl}$   
 Reaction with group-IA amalgam:  
 5.5.3.2.1
- $\text{C}_{19}\text{H}_{15}\text{Cl}_2\text{LiPb}$**   
 $(\text{C}_6\text{H}_5)_3\text{PbCCl}_2\text{Li}$   
 Formation: 5.5.2.3.1
- $\text{C}_{19}\text{H}_{15}\text{Cs}$**   
 $\text{Cs}[(\text{C}_6\text{H}_5)_3\text{C}]$   
 Formation: 5.5.3.2.1
- $\text{C}_{19}\text{H}_{15}\text{K}$**   
 $\text{K}[(\text{C}_6\text{H}_5)_3\text{C}]$   
 Formation: 5.5.3.2.5, 5.5.3.2.6, 5.5.3.3.1



- Reaction with RX: 5.5.3.2.5
- C<sub>19</sub>H<sub>15</sub>K<sub>2</sub>**  
 $\text{K}_2[\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_4\text{CCHC}_6\text{H}_5]$   
 Formation: 5.5.3.2.6
- C<sub>19</sub>H<sub>15</sub>Li**  
 $(\text{C}_6\text{H}_5)_3\text{CLi}$   
 Formation: 5.5.2.2.1, 5.5.2.2.4, 5.5.2.2.5, 5.5.2.3.5
- C<sub>19</sub>H<sub>15</sub>LiO**  
 $(\text{C}_6\text{H}_5)_2\text{C}(\text{OC}_6\text{H}_5)\text{Li}$   
 Formation: 5.5.2.2.5
- C<sub>19</sub>H<sub>15</sub>LiS<sub>3</sub>**  
 $(\text{C}_6\text{H}_5\text{S})_3\text{CLi}$   
 Formation: 5.5.2.3.2
- C<sub>19</sub>H<sub>15</sub>LiSe<sub>3</sub>**  
 $(\text{C}_6\text{H}_5\text{Se})_3\text{CLi}$   
 Formation: 5.5.2.3.1, 5.5.2.3.2
- C<sub>19</sub>H<sub>15</sub>Li<sub>2</sub>N**  
 $\text{C}_6\text{H}_5\text{C}(\text{Li})[\text{N}(\text{C}_6\text{H}_5)\text{Li}]\text{C}_6\text{H}_5$   
 Formation: 5.5.2.2.3
- C<sub>19</sub>H<sub>15</sub>N**  
 $\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)\text{C}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.3
- C<sub>19</sub>H<sub>15</sub>Na**  
 $\text{Na}[(\text{C}_6\text{H}_5)_3\text{C}]$   
 Addition to olefins: 5.5.3.3.3  
 Formation: 5.5.3.2.1, 5.5.3.2.5, 5.5.3.2.6, 5.5.3.3.1
- C<sub>19</sub>H<sub>15</sub>Rb**  
 $\text{Rb}[(\text{C}_6\text{H}_5)_3\text{C}]$   
 Formation: 5.5.3.2.1
- C<sub>19</sub>H<sub>16</sub>BrHgP**  
 $[\text{o}-(\text{C}_6\text{H}_5)_2\text{PCH}_2]\text{C}_6\text{H}_4\text{HgBr}$   
 Formation: 5.7.2.3.1
- C<sub>19</sub>H<sub>16</sub>Br<sub>2</sub>CuHgP**  
 $\text{o-BrHgC}_6\text{H}_4\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2 \cdot \text{CuBr}$   
 Formation: 5.7.2.3.1
- C<sub>19</sub>H<sub>16</sub>LiOPS**  
 $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}(\text{Li})\text{SC}_6\text{H}_5$   
 Formation: 5.5.2.3.2
- C<sub>19</sub>H<sub>16</sub>LiP**  
 $\text{CH}_2=\text{P}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{Li-o}$   
 Formation: 5.5.2.3.2  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>19</sub>H<sub>16</sub>S**  
 $(\text{C}_6\text{H}_5)_2\text{CHSC}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.5
- C<sub>19</sub>H<sub>16</sub>S<sub>2</sub>**  
 $\text{C}_6\text{H}_5\text{CH}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion: 5.5.2.2.5
- C<sub>19</sub>H<sub>16</sub>Se<sub>3</sub>**  
 $(\text{C}_6\text{H}_5\text{Se})_3\text{CH}$   
 Transmetallation: 5.5.2.3.1
- C<sub>19</sub>H<sub>17</sub>GeLi**  
 $(\text{C}_6\text{H}_5)_3\text{GeCH}_2\text{Li}$   
 Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>19</sub>H<sub>17</sub>LiPb**  
 $(\text{C}_6\text{H}_5)_3\text{PbCH}_2\text{Li}$   
 Formation: 5.5.2.3.1, 5.5.2.3.3
- C<sub>19</sub>H<sub>17</sub>LiSn**  
 $(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{Li}$   
 Formation: 5.5.2.3.3
- C<sub>19</sub>H<sub>18</sub>AuP**  
 $\text{CH}_3\text{Au} \cdot \text{PPh}_3$   
 Formation: 5.6.4, 5.6.4.3  
 Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>19</sub>H<sub>20</sub>Ge**  
 $\text{i-C}_3\text{H}_7(1-\text{C}_{10}\text{H}_7)(\text{C}_6\text{H}_5)\text{GeH}$   
 Reaction with RLi: 5.5.5.4
- C<sub>19</sub>H<sub>20</sub>S<sub>2</sub>**  
 $\text{CH}_2(\text{CH}_2)_4\text{C}=\text{C}(\text{SC}_6\text{H}_5)_2$   
 Reaction with a Li radical anion: 5.5.2.2.5
- C<sub>19</sub>H<sub>22</sub>LiN**  
 $(\text{Z})\text{-o}-(\text{CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4\text{CLi}=\text{C}[\text{C}_6\text{H}_4^* (\text{CH}_3)\text{-p}]\text{CH}_3$   
 Formation: 5.5.2.3.1
- C<sub>19</sub>H<sub>23</sub>LiSe<sub>2</sub>**  
 $(\text{C}_6\text{H}_5\text{Se})_2\text{CLi}(\text{C}_6\text{H}_{13})$   
 Formation: 5.5.2.3.2
- C<sub>19</sub>H<sub>23</sub>Na**  
 $\text{Na}[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2]$   
 Formation: 5.5.3.3.3
- C<sub>19</sub>H<sub>27</sub>K**  
 $\text{K}[[\text{C}(\text{CH}_3)_3\text{CC}\equiv\text{C}]_3\text{C}]$   
 Formation: 5.5.3.2.6
- C<sub>19</sub>H<sub>28</sub>LiPSi<sub>2</sub>**  
 $(\text{C}_6\text{H}_5)_2\text{PC}(\text{Li})[\text{Si}(\text{CH}_3)_3]_2$   
 Formation: 5.5.2.3.2
- C<sub>19</sub>H<sub>30</sub>LiNO**  
 $2,4,6\text{-(i-C}_3\text{H}_7)_3\text{C}_6\text{H}_2\text{COCH}(\text{Li})\text{N}(\text{CH}_3)_2$   
 Formation: 5.5.2.3.2
- C<sub>20</sub>H<sub>5</sub>F<sub>15</sub>GeHg**  
 $(\text{C}_6\text{F}_5)_3\text{GeHgC}_2\text{H}_5$   
 Formation: 5.7.4.2, 5.7.4.5
- C<sub>20</sub>H<sub>12</sub>Li**  
 Li perylene radical anion  
 Formation: 5.5.2.2.3
- C<sub>20</sub>H<sub>12</sub>Li<sub>2</sub>**  
 dilithioperylene  
 Formation: 5.5.2.2.3
- C<sub>20</sub>H<sub>14</sub>Hg**  
 $(1-\text{C}_{10}\text{H}_7)_2\text{Hg}$   
 Formation: 5.7.2.3.6
- C<sub>20</sub>H<sub>14</sub>Li<sub>2</sub>O**  
 $\text{C}_6\text{H}_5\text{C}(\text{Li})\text{CCHCHCHCHCC}(\text{Li})(\text{Ph})\text{O}$   
 Formation: 5.5.2.2.3

- C<sub>20</sub>H<sub>14</sub>Zn**  
(1-C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>Zn  
Reaction with ZnX<sub>2</sub>: 5.7.2.3.2
- C<sub>20</sub>H<sub>15</sub>LiS**  
LiC[S(C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub>C=C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.1
- C<sub>20</sub>H<sub>16</sub>Li<sub>2</sub>O**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(OLi)CH(C<sub>6</sub>H<sub>5</sub>)Li  
Formation: 5.5.2.3.5
- C<sub>20</sub>H<sub>16</sub>Se<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)Se]<sub>2</sub>C=CH(C<sub>6</sub>H<sub>5</sub>)  
Transmetallation: 5.5.2.3.1
- C<sub>20</sub>H<sub>17</sub>Cl**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCH<sub>2</sub>Cl  
Reaction with Na or K metal: 5.5.3.2.1
- C<sub>20</sub>H<sub>17</sub>LiOSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiC(Li)CH<sub>2</sub>O  
Formation: 5.5.2.3.2
- C<sub>20</sub>H<sub>17</sub>LiSn**  
(E)-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH=CHLi  
Formation: 5.5.2.3.1
- C<sub>20</sub>H<sub>17</sub>Na**  
Na[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)]  
Formation: 5.5.3.2.1
- C<sub>20</sub>H<sub>18</sub>Ge**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeCH=CH<sub>2</sub>  
Reaction with PhLi: 5.5.2.3.1
- C<sub>20</sub>H<sub>18</sub>LiN**  
p-[(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>N]C<sub>6</sub>H<sub>4</sub>Li  
Formation: 5.5.2.2.1
- C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>Pb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbOCOCH<sub>3</sub>  
Decomposition: 5.7.6.2
- C<sub>20</sub>H<sub>18</sub>Pb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCH=CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>20</sub>H<sub>18</sub>S**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(CH<sub>3</sub>)SC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5  
Reaction with Na metal: 5.5.3.2.2
- C<sub>20</sub>H<sub>18</sub>Se<sub>3</sub>**  
(C<sub>6</sub>H<sub>5</sub>Se)<sub>3</sub>CCH<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>20</sub>H<sub>18</sub>Si**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiCH=CH<sub>2</sub>  
Reaction with PhLi: 5.5.2.3.1  
Reaction with Li metal: 5.5.2.2.3
- C<sub>20</sub>H<sub>18</sub>Sn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH=CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>20</sub>H<sub>19</sub>ClSi**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>SiCl  
Reaction with Li metal: 5.5.4.2.2, 5.5.4.3
- C<sub>20</sub>H<sub>19</sub>GeLi**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>GeLi  
Formation: 5.5.5.5
- C<sub>20</sub>H<sub>19</sub>LiSi**  
C<sub>6</sub>H<sub>5</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>SiLi  
Formation: 5.5.4.2.2, 5.5.4.3
- C<sub>20</sub>H<sub>20</sub>AuP**  
C<sub>2</sub>H<sub>5</sub>Au·PPh<sub>3</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>20</sub>H<sub>20</sub>F<sub>14</sub>HgO<sub>4</sub>**  
Hg[CH(COBU-t)(COC<sub>3</sub>F<sub>7</sub>-n)]<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>20</sub>H<sub>21</sub>Li**  
(CH<sub>3</sub>)<sub>3</sub>CC≡CC(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>Li  
Formation: 5.5.2.2.1
- C<sub>20</sub>H<sub>22</sub>S<sub>2</sub>**  
CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CHCH=C(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with a Li radical anion.  
5.5.2.2.5
- C<sub>20</sub>H<sub>23</sub>Li**  
CH<sub>2</sub>CH<sub>2</sub>C(n-C<sub>4</sub>H<sub>9</sub>)C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Li  
Formation: 5.5.2.3.4
- C<sub>20</sub>H<sub>24</sub>HgN<sub>2</sub>O<sub>2</sub>**  
[p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N=C(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>20</sub>H<sub>26</sub>Hg**  
[C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>Hg  
Reaction with Li metal: 5.5.2.2.2  
Thermal stability: 5.7.5
- C<sub>20</sub>H<sub>26</sub>Li**  
Li 4,4'-di-t-butylbiphenylide radical anion  
Reaction with RX: 5.5.2.2.1  
[p-(CH<sub>3</sub>)<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>)<sub>3</sub>-p]<sup>-</sup>Li<sup>+</sup>  
Lithiating agent: 5.5.2.3.5
- C<sub>20</sub>H<sub>30</sub>HgSi<sub>2</sub>**  
[C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>Hg  
Reaction with Li metal: 5.5.2.2.2
- C<sub>20</sub>H<sub>30</sub>Si<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SiSi(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.4.2.1
- C<sub>20</sub>H<sub>31</sub>B**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>B(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>  
Formation: 5.7.2.3.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>20</sub>H<sub>32</sub>CuNP**  
NCCCH<sub>2</sub>Cu·PPh<sub>3</sub>  
Formation: 5.6.4.5
- C<sub>20</sub>H<sub>32</sub>LiNO**  
2,4,6-(i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(O)N(C<sub>2</sub>H<sub>5</sub>)CH(C\*H<sub>3</sub>)Li  
Formation: 5.5.2.3.2

- C<sub>26</sub>H<sub>33</sub>HgNO<sub>2</sub>**  
 $n\text{-C}_{10}\text{H}_{21}\text{CH}(\text{HNC}_6\text{H}_5)\text{CH}_2\text{HgOC}(\text{O})\text{C}^*$   
 $\text{H}_3$   
 Formation: 5.7.2.3.3
- C<sub>20</sub>H<sub>40</sub>O<sub>2</sub>Sn**  
 $(\text{E})\text{-(n-C}_4\text{H}_9)_3\text{SnCH=CHCH}_2\text{O}\overline{\text{CHO}}(\text{C}^*$   
 $\text{H}_2)_3\text{CH}_2$   
 Transmetallation: 5.5.2.3.1
- C<sub>20</sub>H<sub>42</sub>Hg**  
 $(n\text{-C}_{10}\text{H}_{21})_2\text{Hg}$   
 Formation: 5.7.2.2.1
- C<sub>20</sub>H<sub>44</sub>OSn**  
 $(n\text{-C}_4\text{H}_9)_3\text{SnCH}(\text{OCH}_3)\text{C}_6\text{H}_{13}$   
 Transmetallation: 5.5.2.3.1
- C<sub>20</sub>H<sub>54</sub>CdSi<sub>6</sub>**  
 $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Cd}$   
 Formation: 5.7.2.3.1
- C<sub>20</sub>H<sub>54</sub>Si<sub>6</sub>Zn**  
 $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Zn}$   
 Formation: 5.7.2.3.1
- C<sub>21</sub>H<sub>15</sub>CrLiO<sub>4</sub>S**  
 $(\text{CO})_3\text{Cr}[\overline{\text{CH=CPhCH=CPhCH=S}}(\text{O})^*\text{CH}_2\text{Li}]$   
 Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>15</sub>LiMoO<sub>4</sub>S**  
 $(\text{CO})_3\text{Mo}[\overline{\text{CH=CPhCH=CPh}^*}$   
 $\text{CH=S}(\text{O})\text{CH}_2\text{Li}]$   
 Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>15</sub>LiO<sub>4</sub>SW**  
 $(\text{CO})_3\text{W}[\overline{\text{CH=CPhCH=CPh}^*}$   
 $\text{CH=S}(\text{O})\text{CH}_2\text{Li}]$   
 Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>15</sub>Na**  
 $\text{Na}[\overline{\text{C}(\text{CH}_3)_4\text{CC}(\text{Ph})\text{CHC}(\text{Ph})}]$   
 Formation: 5.5.3.2.6
- C<sub>21</sub>H<sub>17</sub>Li**  
 $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CH}(\text{Li})\text{C}_6\text{H}_5$   
 Reaction with Li metal: 5.5.2.2.3
- C<sub>21</sub>H<sub>17</sub>LiOS**  
 $\overline{\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{C}(\text{Li})\text{SOC}_6\text{H}_5}$   
 Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>17</sub>LiO<sub>2</sub>S**  
 $\overline{\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{C}(\text{SO}_2\text{C}_6\text{H}_5)\text{Li}}$   
 Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>17</sub>LiS**  
 $\overline{\text{CH}(\text{C}_6\text{H}_5)\text{CH}(\text{C}_6\text{H}_5)\text{C}(\text{SC}_6\text{H}_5)\text{Li}}$   
 Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>17</sub>Li<sub>3</sub>**  
 $\text{C}_6\text{H}_5\text{CH}(\text{Li})\text{C}(\text{Li})(\text{C}_6\text{H}_5)\text{CH}(\text{Li})\text{C}_6\text{H}_5$   
 Formation: 5.5.2.2.3
- C<sub>21</sub>H<sub>18</sub>Cl<sub>2</sub>Pb**  
 $(\text{C}_6\text{H}_5)_3\text{PbCH}_2\text{CH}=\text{CH}=\text{CCl}_2$   
 Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>19</sub>ClPb**  
 $(\text{C}_6\text{H}_5)_3\text{PbCH}_2\text{CH}=\text{CHCl}$   
 Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>19</sub>Cs**  
 $\text{Cs}[\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2]$   
 Formation: 5.5.3.3.2
- C<sub>21</sub>H<sub>19</sub>K**  
 $\text{K}[\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2]$   
 Formation: 5.5.3.3.2
- C<sub>21</sub>H<sub>19</sub>Li**  
 $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Li}$   
 Substrate in metal-metal exchange:  
 5.5.3.3.2
- C<sub>21</sub>H<sub>19</sub>Na**  
 $\text{Na}[\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2]$   
 Formation: 5.5.3.3.2
- C<sub>21</sub>H<sub>20</sub>OSn**  
 $(\text{C}_6\text{H}_5)_3\text{SnCH}=\text{CHCH}_2\text{OH}$   
 Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>20</sub>Si**  
 $\text{cyclo-C}_3\text{H}_5(\text{C}_6\text{H}_5)_3\text{Si}$   
 Reaction with Li metal: 5.5.4.5
- C<sub>21</sub>H<sub>20</sub>Sn**  
 $(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{CH}=\text{CH}_2$   
 Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>21</sub>B**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{B}$   
 Reactions with R<sub>2</sub>Zn: 5.7.2.4.3  
 $(2\text{-CH}_3\text{C}_6\text{H}_4)_3\text{B}$   
 Reactions with R<sub>2</sub>Zn: 5.7.2.4.3
- C<sub>21</sub>H<sub>21</sub>Bi**  
 $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{Bi}$   
 Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>21</sub>BrSn**  
 $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SnBr}$   
 Reaction with R<sub>3</sub>SnK: 5.5.6.2.3
- C<sub>21</sub>H<sub>21</sub>ClPb**  
 $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{PbCl}$   
 Reaction with Li metal: 5.5.7.4
- C<sub>21</sub>H<sub>21</sub>ClSi**  
 $(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{SiCl}$   
 Reaction with Na-K: 5.5.4.2.2, 5.5.4.3
- C<sub>21</sub>H<sub>21</sub>ClSn**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnCl}$   
 Reaction with RLi: 5.5.2.3.1  
 Reaction with Li metal: 5.5.2.2.2
- C<sub>21</sub>H<sub>21</sub>GeLi**  
 $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{GeLi}$   
 Formation: 5.5.5.5

- C<sub>21</sub>H<sub>21</sub>KSi**  
K[(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Si]  
Formation: 5.5.4.3, 5.5.4.2.1, 5.5.4.2.2
- C<sub>21</sub>H<sub>21</sub>LiPb**  
(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PbLi  
Formation: 5.5.7.2.1, 5.5.7.4
- C<sub>21</sub>H<sub>21</sub>LiSn**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>SnLi  
Formation: 5.5.6.3.1
- C<sub>21</sub>H<sub>21</sub>NaO<sub>3</sub>Pb**  
Na[(o-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.2.1, 5.5.7.4
- C<sub>21</sub>H<sub>21</sub>NaPb**  
Na[(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.2.1, 5.5.7.4
- C<sub>21</sub>H<sub>21</sub>Sb**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>Sb  
Transmetallation: 5.5.2.3.1  
(m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb  
Transmetallation: 5.5.2.3.1  
(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb  
Transmetallation: 5.5.2.3.1  
(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb  
Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>22</sub>Ge**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>GeH  
Reaction with RLi: 5.5.5.4
- C<sub>21</sub>H<sub>22</sub>GeO<sub>3</sub>**  
(3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>GeH  
Reaction with RLi: 5.5.5.4  
(4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>GeH  
Reaction with Li metal: 5.5.5.4
- C<sub>21</sub>H<sub>22</sub>LiNO**  
cis-(cyclo-C<sub>6</sub>H<sub>11</sub>CHC(H<sub>3</sub>C(Li))COC<sub>6</sub>H<sub>5</sub>)  
Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>22</sub>Si**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>SiH  
Reaction with R<sub>3</sub>SiH: 5.7.3.3
- C<sub>21</sub>H<sub>24</sub>AuGeP**  
(CH<sub>3</sub>)<sub>3</sub>GeAu · PPh<sub>3</sub>  
Formation: 5.6.5.3
- C<sub>21</sub>H<sub>24</sub>Si<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiSi(CH<sub>3</sub>)<sub>3</sub>  
Reaction with Na-K: 5.5.4.2.1
- C<sub>21</sub>H<sub>27</sub>LiSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si[CH\*  
Li(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>]CH<sub>2</sub>CH=CH<sub>2</sub>  
Formation: 5.5.2.3.4  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(CH<sub>2</sub>CH=CH<sub>2</sub>)CHLiCH<sub>2</sub>C<sub>4</sub>H<sub>9</sub>  
Formation: 5.5.2.3.2
- C<sub>21</sub>H<sub>37</sub>NSn**  
(Z)-(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH=CHN(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>39</sub>NSn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH<sub>2</sub>N(CH<sub>3</sub>)CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>40</sub>O<sub>3</sub>Sn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH(CCHOCHCH)OCH(C\*  
H<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>44</sub>OSn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH<sub>2</sub>OCH(n-C<sub>4</sub>H<sub>9</sub>)C(C\*  
H<sub>3</sub>)=CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>21</sub>H<sub>51</sub>LiO<sub>3</sub>Si<sub>4</sub>**  
[(CH<sub>3</sub>)<sub>3</sub>Si]<sub>3</sub>SiLi · 3 CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>  
Formation: 5.5.3.3.3
- C<sub>21</sub>H<sub>57</sub>HgLiO<sub>6</sub>Si<sub>3</sub>**  
[Li(H<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>][(Me<sub>3</sub>Si)<sub>3</sub>Hg]  
Formation: 5.7.3.1
- C<sub>22</sub>H<sub>10</sub>F<sub>10</sub>HgN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**  
(C<sub>6</sub>F<sub>5</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7
- C<sub>22</sub>H<sub>10</sub>HgN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**  
(C<sub>6</sub>Cl<sub>5</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7
- C<sub>22</sub>H<sub>12</sub>Cl<sub>8</sub>HgN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**  
(m-HC<sub>6</sub>Cl<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7  
(o-HC<sub>6</sub>Cl<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7  
(p-HC<sub>6</sub>Cl<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7
- C<sub>22</sub>H<sub>12</sub>F<sub>8</sub>HgN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**  
(m-HC<sub>6</sub>F<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7  
(o-HC<sub>6</sub>F<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7  
(p-HC<sub>6</sub>F<sub>4</sub>SO<sub>3</sub>)<sub>2</sub>Hg · 2 NC<sub>5</sub>H<sub>5</sub>  
Desulfonation: 5.7.2.3.7
- C<sub>22</sub>H<sub>14</sub>Li<sub>2</sub>**  
dilithiopentacene  
Formation: 5.5.2.2.3
- C<sub>22</sub>H<sub>21</sub>ClPb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCH<sub>2</sub>CH=CClCH<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>22</sub>H<sub>22</sub>HgO<sub>2</sub>**  
[m-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>C≡C]<sub>2</sub>Hg  
Reaction with Li metal: 5.5.2.2.2
- C<sub>22</sub>H<sub>22</sub>OSn**  
(Z)-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH=CHOC<sub>2</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>22</sub>H<sub>22</sub>S<sub>2</sub>**  
p-(C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>  
Reaction with Li metal: 5.5.2.2.5

- C<sub>22</sub>H<sub>22</sub>Sn**  
 $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>22</sub>H<sub>25</sub>LiPbSi**  
 $(\text{C}_6\text{H}_5)_3\text{PbCHLiSi}(\text{CH}_3)_3$   
 Formation: 5.5.2.3.1
- C<sub>22</sub>H<sub>30</sub>Cu<sub>2</sub>N<sub>4</sub>**  
 $[\text{CuC}(=\text{NCH}_3)\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2]_2$   
 Formation: 5.6.4.4
- C<sub>22</sub>H<sub>34</sub>Si<sub>2</sub>**  
 $(\text{CH}_3)_3\text{SiCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Si}^*$   
 $(\text{CH}_3)_3$   
 Formation: 5.5.2.2.3
- C<sub>22</sub>H<sub>38</sub>HgO<sub>4</sub>**  
 $\text{Hg}[\text{CH}[\text{COC}(\text{CH}_3)_3]_2]_2$   
 Formation: 5.7.2.3.4  
 Reaction with  $\text{HgX}_2$ : 5.7.2.3.2
- C<sub>22</sub>H<sub>48</sub>O<sub>2</sub>Sn**  
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}(\text{C}_5\text{H}_{11})\text{OCH}(\text{CH}_3)\text{OC}_2^*\text{H}_5$   
 Transmetallation: 5.5.2.3.1
- C<sub>23</sub>H<sub>17</sub>LiN**  
 $[\text{C}_6\text{H}_5\text{CCHC}(\text{C}_6\text{H}_5)\text{CHC}(\text{C}_6\text{H}_5)\text{N}]^-\text{Li}^+$   
 Formation: 5.5.2.2.3
- C<sub>23</sub>H<sub>17</sub>Li<sub>2</sub>N**  
 $[\text{PhCCHCPhCHC}(\text{C}_6\text{H}_5)\text{N}]^{2-} 2\text{Li}^+$   
 Formation: 5.5.2.2.3
- C<sub>23</sub>H<sub>19</sub>Li**  
 $[\text{C}_6\text{H}_5\text{CH}::\text{CH}::\text{C}(\text{C}_6\text{H}_5)::\text{CH}::\text{CH}^*\text{C}_6\text{H}_5]^- \text{Li}^+$   
 Formation: 5.5.2.3.2
- C<sub>23</sub>H<sub>20</sub>AgP**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Ag} \cdot \text{PPh}_3$   
 Formation: 5.6.4, 5.6.4.1
- C<sub>23</sub>H<sub>20</sub>AuP**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Au} \cdot \text{PPh}_3$   
 Formation: 5.6.4
- C<sub>23</sub>H<sub>20</sub>CuP**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Cu} \cdot \text{PPh}_3$   
 Formation: 5.6.4, 5.6.4.1
- C<sub>23</sub>H<sub>20</sub>FeLiOP**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Fe}[\text{C}_5\text{H}_4\text{CH}(\text{Li})\text{P}(\text{O})(\text{C}_6\text{H}_5)_2]\text{-h}^5$   
 Formation: 5.5.2.3.2
- C<sub>23</sub>H<sub>20</sub>FeLiPS**  
 $\text{h}^5\text{-C}_5\text{H}_5\text{Fe}[\text{C}_5\text{H}_4\text{CH}(\text{Li})\text{P}(\text{S})(\text{C}_6\text{H}_5)_2]\text{-h}^5$   
 Formation: 5.5.2.3.2
- C<sub>23</sub>H<sub>21</sub>AuNO<sub>2</sub>P**  
 $\text{Au}(\text{PPh}_3)[\text{C}(\text{H})(\text{CN})\text{C}(\text{O})\text{OC}_2\text{H}_5]$   
 Formation: 5.6.4.3
- C<sub>23</sub>H<sub>21</sub>K**  
 $\text{K}[\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_5)=\text{CC}_6\text{H}_5]$   
 Formation: 5.5.3.3.3
- 10-(2-Phenyl-2methlethyl)-9-potassio-9,10-Bihydroanthracene  
 Formation: 5.5.3.3.3
- C<sub>23</sub>H<sub>21</sub>Na**  
 $\text{Na}[(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{CH}=\text{CHCH}_2]$   
 Formation: 5.5.3.3.3
- C<sub>23</sub>H<sub>23</sub>K**  
 $\text{K}[\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2]$   
 Formation: 5.5.3.3.3
- C<sub>23</sub>H<sub>24</sub>SSn**  
 $(\text{CH}_3)_3\text{SnC}[\text{S}(\text{C}_6\text{H}_5)]=\text{C}(\text{C}_6\text{H}_5)_2$   
 Transmetallation: 5.5.2.3.1
- C<sub>23</sub>H<sub>26</sub>SiSn**  
 $(\text{E})\text{-(CH}_3)_3\text{SiCH}=\text{CHSn}(\text{C}_6\text{H}_5)_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>23</sub>H<sub>36</sub>Sn**  
 1-Naphthyl-Sn( $\text{C}_4\text{H}_9\text{-n}$ )<sub>3</sub>  
 Metal exchange with RNa and RK: 5.5.3.3.2  
 2-Naphthyl-Sn( $\text{C}_4\text{H}_9\text{-n}$ )<sub>3</sub>  
 Metal exchange with RNa and RK: 5.5.3.3.2
- C<sub>23</sub>H<sub>42</sub>O<sub>2</sub>Sn**  
 $\text{C}_2\text{H}_5\text{CH}[\text{SnBu}_3]\text{OCH}_2\text{OCH}_2\text{C}_6\text{H}_5$   
 Transmetallation: 5.5.2.3.1  
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}(\text{C}_6\text{H}_5)\text{OCH}(\text{CH}_3)\text{OC}_2\text{H}_5$   
 Transmetallation: 5.5.2.3.1
- C<sub>23</sub>H<sub>48</sub>O<sub>2</sub>Sn**  
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}(\text{cyclo-C}_6\text{H}_{11})\text{OCH}(\text{CH}_3)^*\text{OC}_2\text{H}_5$   
 Transmetallation: 5.5.2.3.1
- C<sub>23</sub>H<sub>50</sub>OSiSn**  
 $(\text{E})\text{-(n-C}_4\text{H}_9)_3\text{SnCH}=\text{CHCH}(\text{C}_5\text{H}_{11})^*\text{OSi}(\text{CH}_3)_3$   
 Transmetallation: 5.5.2.3.1
- C<sub>23</sub>H<sub>50</sub>O<sub>2</sub>Sn**  
 $(\text{n-C}_4\text{H}_9)_3\text{SnCH}(\text{C}_6\text{H}_{13})\text{OCH}(\text{CH}_3)^*\text{OC}_2\text{H}_5$   
 Transmetallation: 5.5.2.3.1
- C<sub>24</sub>Br<sub>2</sub>F<sub>20</sub>Ge<sub>2</sub>**  
 $[(\text{C}_6\text{F}_5)_2\text{BrGe}]_2$   
 Formation: 5.7.4.2
- C<sub>24</sub>Cs**  
 $\text{CsC}_{24}$   
 Formation: 5.5.3.1.2
- C<sub>24</sub>Cu<sub>4</sub>F<sub>20</sub>**  
 $[\text{CuC}_6\text{F}_5]_4$   
 Interaggregate Exchange: 5.6.4.1
- C<sub>24</sub>F<sub>20</sub>Ge**  
 $(\text{C}_6\text{F}_5)_4\text{Ge}$   
 Reaction with Li metal: 5.5.5.5

- C<sub>24</sub>F<sub>20</sub>Zr**  
(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Zr  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>24</sub>H<sub>15</sub>AuCl<sub>2</sub>F<sub>5</sub>**  
cis-C<sub>6</sub>F<sub>5</sub>AuCl<sub>2</sub> · PPh<sub>3</sub>  
Formation: 5.6.4.1
- C<sub>24</sub>H<sub>15</sub>AuF<sub>5</sub>P**  
C<sub>6</sub>F<sub>5</sub>Au · PPh<sub>3</sub>  
Formation: 5.6.4.1
- C<sub>24</sub>H<sub>15</sub>F<sub>15</sub>Ge<sub>2</sub>**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeGe(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Reaction with HgX<sub>2</sub>: 5.7.4.5  
Reaction with RHgCl: 5.7.4.5
- C<sub>24</sub>H<sub>15</sub>F<sub>15</sub>Ge<sub>2</sub>Hg**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeHgGe(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>  
Formation: 5.7.4.6  
Reaction with Ph<sub>3</sub>SnBr: 5.7.5.3
- C<sub>24</sub>H<sub>18</sub>Hg**  
(o-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg  
Reaction with Li metal: 5.5.2.2.2
- C<sub>24</sub>H<sub>20</sub>AuP**  
C<sub>6</sub>H<sub>5</sub>Au · PPh<sub>3</sub>  
Formation: 5.6.4, 5.6.4.1, 5.6.4.3, 5.6.5.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>24</sub>H<sub>20</sub>BrSb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>SbBr  
Reaction with RLi: 5.5.2.3.1
- C<sub>24</sub>H<sub>20</sub>Br<sub>2</sub>Ge<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>BrGe]<sub>2</sub>  
Formation: 5.7.4.2
- C<sub>24</sub>H<sub>20</sub>Ge**  
(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Ge  
Reaction with Li or Na-K: 5.5.5.5
- C<sub>24</sub>H<sub>20</sub>Ge<sub>2</sub>Li<sub>2</sub>**  
Li(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>GeGe(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Li  
Formation: 5.5.5.4
- C<sub>24</sub>H<sub>20</sub>Pb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Pb  
Formation: 5.5.7.2.2  
Reaction with group-IA metals: 5.5.7.3
- C<sub>24</sub>H<sub>20</sub>Si**  
(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Si  
Formation: 5.5.2.3.4, 5.7.3.1  
Reaction with Li metal: 5.5.4.5  
Reaction with Na-K: 5.5.4.5
- C<sub>24</sub>H<sub>20</sub>Sn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Sn  
Formation: 5.7.5.1.1  
Reaction with Na[C<sub>10</sub>H<sub>8</sub>]<sup>-</sup>: 5.5.6.5  
Transmetallation: 5.5.2.3.1
- C<sub>24</sub>H<sub>22</sub>Ge<sub>2</sub>**  
Ge(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>HGeH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with R<sub>2</sub>Hg: 5.7.4.2
- Reaction with Li-Hg: 5.5.5.2.2
- C<sub>24</sub>H<sub>25</sub>Si<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>HSiSiH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with Li metal: 5.5.4.2.1
- C<sub>24</sub>H<sub>27</sub>B**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>B  
Formation: 5.7.2.3.1  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>24</sub>H<sub>27</sub>BiO<sub>3</sub>**  
(o-C<sub>2</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Bi  
Transmetallation: 5.5.2.3.1
- C<sub>24</sub>H<sub>27</sub>ClPbSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCH<sub>2</sub>CH=CCSi(CH<sub>3</sub>)<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>24</sub>H<sub>27</sub>NaO<sub>3</sub>Pb**  
Na[(p-C<sub>2</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Pb]  
Formation: 5.5.7.2.1, 5.5.7.4
- C<sub>24</sub>H<sub>30</sub>GeSi**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Si<sub>4</sub>Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
Reaction with Li metal: 5.5.4.2.1
- C<sub>24</sub>H<sub>30</sub>HgSi<sub>2</sub>**  
(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiH<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
Formation: 5.7.3.3  
Randomization: 5.7.3.3
- C<sub>24</sub>H<sub>30</sub>Sn<sub>2</sub>**  
(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnSn(CH<sub>3</sub>)<sub>3</sub>  
Formation: 5.5.6.2.3
- C<sub>24</sub>H<sub>35</sub>LiO<sub>5</sub>SSi**  
(CH<sub>3</sub>)<sub>3</sub>SiLi(SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)CH(CH<sub>3</sub>)CH(C\*  
H<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)OCH<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>OCH<sub>3</sub>  
Formation: 5.5.2.3.4
- C<sub>24</sub>H<sub>38</sub>Ge<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>(i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>GeGe(i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.5.2.1
- C<sub>24</sub>H<sub>38</sub>Si<sub>2</sub>**  
C<sub>5</sub>H<sub>11</sub>(C<sub>6</sub>H<sub>5</sub>)CH<sub>3</sub>SiSiCH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)C<sub>5</sub>H<sub>11</sub>  
Reaction with Li metal: 5.5.4.2.1  
C<sub>6</sub>H<sub>5</sub>(i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>SiSi(i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.4.2.1
- C<sub>24</sub>H<sub>44</sub>O<sub>2</sub>Sn**  
PhCH<sub>2</sub>CH(CH<sub>3</sub>)CH(SnBu<sub>3</sub>)OCH<sub>2</sub>OMe  
Transmetallation: 5.5.2.3.1
- C<sub>24</sub>H<sub>44</sub>O<sub>3</sub>Sn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH[C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-m]OCH(C\*  
H<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH(C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-p)OCH(C\*  
H<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>24</sub>H<sub>48</sub>OSiSn**  
 $\overline{(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{SiOC}=\text{CH}(\text{CH}_2)_2\text{C}[\text{Sn}^*]}$   
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>=CH  
Transmetallation: 5.5.2.3.1

- C<sub>24</sub>H<sub>50</sub>Hg**  
(n-C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>24</sub>H<sub>52</sub>OSiSn**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH=CHCH<sub>2</sub>C(CH<sub>3</sub>)(n-C<sub>4</sub>\*  
H<sub>9</sub>)OSi(CH<sub>3</sub>)<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>24</sub>H<sub>54</sub>CdSi<sub>2</sub>**  
[(Me<sub>3</sub>C)<sub>3</sub>Si]<sub>2</sub>Cd  
Formation: 5.7.3.3
- C<sub>24</sub>H<sub>54</sub>HgSi<sub>2</sub>**  
[(Me<sub>3</sub>C)<sub>3</sub>Si]<sub>2</sub>Hg  
Formation: 5.7.3.3
- C<sub>24</sub>H<sub>54</sub>HgSn<sub>2</sub>**  
[(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
Formation: 5.7.5.4  
[(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
Formation: 5.7.5.2.3  
[(t-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
Formation: 5.7.5.2.3  
Thermal stability: 5.7.5
- C<sub>24</sub>H<sub>54</sub>Sn<sub>2</sub>**  
(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnSn(C<sub>4</sub>H<sub>9</sub>-n)<sub>3</sub>  
Reaction with Li: 5.5.6.2.1  
Reaction with Na naphthalene: 5.5.6.2.2
- C<sub>24</sub>H<sub>60</sub>HgK<sub>2</sub>**  
K<sub>2</sub>[Hg(SiEt<sub>3</sub>)<sub>4</sub>]  
Formation: 5.7.3.5
- C<sub>24</sub>H<sub>66</sub>CdSi<sub>6</sub>Sn<sub>2</sub>**  
[(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Cd  
Formation: 5.7.5.2.2  
Reaction with Hg metal: 5.7.5.1.3
- C<sub>24</sub>H<sub>66</sub>Ge<sub>2</sub>HgSi<sub>6</sub>**  
{[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>Ge}<sub>2</sub>Hg  
Reaction with Li metal: 5.5.5.6
- C<sub>24</sub>H<sub>66</sub>HgSi<sub>2</sub>**  
[(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Si]<sub>2</sub>Hg  
Formation: 5.7.3.4
- C<sub>24</sub>H<sub>66</sub>HgSi<sub>6</sub>Sn<sub>2</sub>**  
{[(CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>]<sub>3</sub>Sn}<sub>2</sub>Hg  
Reaction with Li metal: 5.5.6  
[(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
Formation: 5.7.5.1.3, 5.7.5.2.3  
Oxidation in air: 5.7.5.2.3
- C<sub>24</sub>H<sub>66</sub>OSi<sub>6</sub>Sn<sub>2</sub>**  
[(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>O  
Formation: 5.7.5.2.3
- C<sub>24</sub>K**  
KC<sub>24</sub>  
Formation: 5.5.3.1.2
- C<sub>24</sub>Rb**  
RbC<sub>24</sub>  
Formation: 5.5.3.1.2
- C<sub>25</sub>H<sub>15</sub>AuF<sub>5</sub>O<sub>2</sub>P**  
AuO<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>·PPh<sub>3</sub>  
Decarboxylation: 5.6.4.5
- C<sub>25</sub>H<sub>19</sub>Na**  
Na[(p-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]  
Formation: 5.5.3.2.6
- C<sub>25</sub>H<sub>20</sub>Cl<sub>2</sub>HgPb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCCl<sub>2</sub>HgC<sub>6</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>25</sub>H<sub>20</sub>S**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CSC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>25</sub>H<sub>20</sub>S<sub>4</sub>**  
(C<sub>6</sub>H<sub>5</sub>S)<sub>4</sub>C  
Transmetallation: 5.5.2.3.1
- C<sub>25</sub>H<sub>20</sub>Se<sub>4</sub>**  
(C<sub>6</sub>H<sub>5</sub>Se)<sub>4</sub>C  
Transmetallation: 5.5.2.3.1
- C<sub>25</sub>H<sub>21</sub>As<sub>2</sub>Li**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>As]<sub>2</sub>CHLi  
Formation: 5.5.2.3.2
- C<sub>25</sub>H<sub>21</sub>BrHgO<sub>2</sub>P<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)]<sub>2</sub>CHHgBr  
Formation: 5.7.2.3.1
- C<sub>25</sub>H<sub>21</sub>LiO<sub>2</sub>P<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(O)]<sub>2</sub>CHLi  
Formation: 5.5.2.3.2  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>25</sub>H<sub>21</sub>LiP<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P]<sub>2</sub>CHLi  
Formation: 5.5.2.3.2
- C<sub>25</sub>H<sub>21</sub>LiSb<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sb]<sub>2</sub>CHLi  
Formation: 5.5.2.3.2
- C<sub>25</sub>H<sub>22</sub>As<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>As]<sub>2</sub>CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>25</sub>H<sub>22</sub>AuP**  
AuC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4·PPh<sub>3</sub>  
Reaction with HBF<sub>4</sub>: 5.6.4.3
- C<sub>25</sub>H<sub>22</sub>P<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with CuR: 5.6.4.3
- C<sub>25</sub>H<sub>22</sub>Sb<sub>2</sub>**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sb]<sub>2</sub>CH<sub>2</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>25</sub>H<sub>22</sub>Si**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>25</sub>H<sub>22</sub>Sn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Transmetallation: 5.5.2.3.1

- C<sub>25</sub>H<sub>23</sub>LiSi<sub>2</sub>**  
CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Si<sub>2</sub>Li  
Formation: 5.5.4.2.2
- C<sub>26</sub>F<sub>24</sub>Hg<sub>8</sub>O<sub>16</sub>**  
C<sub>10</sub>(HgO<sub>2</sub>CCF<sub>3</sub>)<sub>8</sub>  
Formation: 5.7.2.3.4
- C<sub>26</sub>H<sub>18</sub>Li<sub>2</sub>**  
dilithio-9,10-diphenylphenanthrene  
Formation: 5.5.2.2.3
- C<sub>26</sub>H<sub>18</sub>Zn**  
(C<sub>13</sub>H<sub>9</sub>)<sub>2</sub>Zn  
Formation: 5.7.2.4.1
- C<sub>26</sub>H<sub>20</sub>Cl<sub>2</sub>Hg**  
ClHgC(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cl  
Formation: 5.7.2.3.3
- C<sub>26</sub>H<sub>20</sub>HgN<sub>4</sub>O<sub>2</sub>P<sub>2</sub>**  
Hg[C(N<sub>2</sub>)P(O)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>  
Formation: 5.7.2.3.4
- C<sub>26</sub>H<sub>20</sub>Li**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sup>-</sup>Li<sup>+</sup>  
Formation: 5.5.2.2.3
- C<sub>26</sub>H<sub>20</sub>Li<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(Li)C(Li)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.2.3
- C<sub>26</sub>H<sub>22</sub>AuP**  
trans-C<sub>6</sub>H<sub>5</sub>CH=CHAu · PPh<sub>3</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>26</sub>H<sub>22</sub>HgS<sub>4</sub>**  
[(C<sub>6</sub>H<sub>5</sub>S)<sub>2</sub>CH]<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>26</sub>H<sub>22</sub>Si**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiCH=CH(C<sub>6</sub>H<sub>5</sub>)  
Transmetallation: 5.5.2.3.1
- C<sub>26</sub>H<sub>22</sub>Zn**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH]<sub>2</sub>Zn  
Formation: 5.7.2.3.1
- C<sub>26</sub>H<sub>23</sub>GeLi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeCH(Li)CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1, 5.5.2.3.4
- C<sub>26</sub>H<sub>23</sub>LiSi**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiCH(Li)CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Formation: 5.5.2.3.1
- C<sub>26</sub>H<sub>24</sub>Ge**  
C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
Reaction with Li metal: 5.5.5.5
- C<sub>26</sub>H<sub>24</sub>SSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p  
Transmetallation: 5.5.2.3.1
- C<sub>26</sub>H<sub>26</sub>LiO<sub>4</sub>P**  
Ph<sub>3</sub>P=C(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)CH(Li)CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>  
Formation: 5.5.2.3.2
- C<sub>26</sub>H<sub>26</sub>Si<sub>2</sub>**  
CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiSi(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>  
Reaction with Li or Na metal: 5.5.4.2.1
- C<sub>26</sub>H<sub>26</sub>Sn<sub>2</sub>Zn**  
[CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sn]<sub>2</sub>Zn  
Formation of TMED complex: 5.7.5.2.1
- C<sub>26</sub>H<sub>34</sub>GeO<sub>3</sub>Zn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeZnC<sub>2</sub>H<sub>5</sub> · O(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>  
Formation: 5.7.4.2
- C<sub>26</sub>H<sub>56</sub>Sn<sub>2</sub>**  
(E)-(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCH=CHSn(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>27</sub>H<sub>26</sub>Si**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiC(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
Reaction with Na-K: 5.5.4.5
- C<sub>27</sub>H<sub>27</sub>AuNP**  
Au(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2) · PPh<sub>3</sub>  
Formation: 5.6.4.1
- C<sub>28</sub>H<sub>16</sub>Cu<sub>4</sub>F<sub>12</sub>**  
[Cu(C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-2)]<sub>4</sub>  
Formation: 5.6.4.1  
Reaction with CuI: 5.6.4.1
- C<sub>28</sub>H<sub>18</sub>Li<sub>4</sub>**  
tetralithio-9,9'-bianthryl  
Formation: 5.5.2.2.3
- C<sub>28</sub>H<sub>20</sub>Li<sub>2</sub>**  
PhC(Li)=C(Ph)C(Ph)=C(Li)Ph  
Formation: 5.5.2.2.3  
1,4-(Ph<sub>4</sub>C<sub>4</sub>)Li<sub>2</sub>  
Reaction with AuCl<sub>3</sub>: 5.6.4.1
- C<sub>28</sub>H<sub>21</sub>AuO**  
C(Ph)C=(Ph)C(Ph)=C(Ph)AuOH  
Formation: 5.6.4.1
- C<sub>28</sub>H<sub>22</sub>Hg**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=CH]<sub>2</sub>Hg  
Reaction with Hg(CN)<sub>2</sub>: 5.7.2.3.2  
[(E)-C<sub>6</sub>H<sub>5</sub>CH=CC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Hg  
Transmetallation: 5.5.2.3.1
- C<sub>28</sub>H<sub>22</sub>Li<sub>2</sub>**  
PhCH(Li)C(Ph)=C(Ph<sub>5</sub>)CH(Li)Ph  
Formation: 5.5.2.2.3
- C<sub>28</sub>H<sub>22</sub>Li<sub>4</sub>**  
PhCH(Li)C(Ph)(Li)C(Ph)(Li)CH(Li)Ph  
Formation: 5.5.2.2.3
- C<sub>28</sub>H<sub>24</sub>AuIP<sub>2</sub>**  
IAuP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Reaction with R<sub>3</sub>GeLi: 5.6.5.1
- C<sub>28</sub>H<sub>24</sub>Li<sub>2</sub>**  
Ph<sub>2</sub>C(Li)CH<sub>2</sub>CH<sub>2</sub>C(Li)Ph<sub>2</sub>  
Formation: 5.5.2.2.3
- C<sub>28</sub>H<sub>28</sub>Cu<sub>4</sub>**  
(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-2)<sub>4</sub>Cu<sub>4</sub>  
Reaction with CNR: 5.6.4.4
- C<sub>28</sub>H<sub>28</sub>Ge**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>4</sub>Ge  
Reaction with Li metal: 5.5.5.5



- C<sub>28</sub>H<sub>28</sub>Pb**  
(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Pb  
Transmetallation: 5.5.2.3.1
- C<sub>28</sub>H<sub>36</sub>Fe<sub>2</sub>HgN<sub>2</sub>**  
[h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.3.1
- C<sub>28</sub>H<sub>76</sub>HgLi<sub>2</sub>O<sub>8</sub>Si<sub>4</sub>**  
[Li<sub>2</sub>(H<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>4</sub>][(Me<sub>3</sub>Si)<sub>4</sub>·Hg]  
Formation: 5.7.3.1
- C<sub>30</sub>H<sub>15</sub>AuClF<sub>10</sub>P**  
Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Cl·PPh<sub>3</sub>  
Formation: 5.6.4
- C<sub>30</sub>H<sub>25</sub>AuCl**  
Au(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cl·PPh<sub>3</sub>  
Formation: 5.6.4.1
- C<sub>30</sub>H<sub>25</sub>LiSi<sub>2</sub>**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiSi(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Li  
Formation: 5.5.4.2.1, 5.5.4.2.2
- C<sub>30</sub>H<sub>26</sub>FeSn**  
h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>CH=CHSn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>-h<sup>5</sup>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>30</sub>H<sub>26</sub>Li<sub>2</sub>Si**  
PhC(Li)C(Ph)=C(Ph)C(Li)(Ph)SiMe<sub>2</sub>  
Formation: 5.5.2.2.3
- C<sub>30</sub>H<sub>26</sub>Li<sub>4</sub>Si**  
PhC(Li)C(Ph)=C(Ph)C(Li)(Ph)SiMe<sub>2</sub>  
Formation: 5.5.2.2.3
- C<sub>30</sub>H<sub>26</sub>Si**  
PhC=C(Ph)C(Ph)=C(Ph)SiMe<sub>2</sub>  
Reaction with Li metal: 5.5.2.2.3
- C<sub>30</sub>H<sub>30</sub>Hg**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>]<sub>2</sub>Hg  
Reaction with Li metal: 5.5.2.2.2
- C<sub>30</sub>H<sub>30</sub>S<sub>2</sub>**  
C<sub>6</sub>H<sub>5</sub>SCH(C<sub>6</sub>H<sub>5</sub>)(CH<sub>2</sub>)<sub>4</sub>CH(C<sub>6</sub>H<sub>5</sub>)SC<sub>6</sub>H<sub>5</sub>  
Reaction with Li metal: 5.5.2.2.5
- C<sub>30</sub>H<sub>33</sub>F<sub>15</sub>Si<sub>3</sub>Sn<sub>2</sub>**  
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>SnSn[CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>  
Formation: 5.7.5
- C<sub>30</sub>H<sub>36</sub>Ag<sub>3</sub>N<sub>3</sub>O<sub>3</sub>**  
[AgC(=NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)OC<sub>2</sub>H<sub>5</sub>]<sub>3</sub>  
Formation: 5.6.4.4
- C<sub>30</sub>H<sub>36</sub>Au<sub>3</sub>N<sub>3</sub>O<sub>3</sub>**  
[AuC(=NC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)-OC<sub>2</sub>H<sub>5</sub>]<sub>3</sub>  
Formation: 5.6.4.4
- C<sub>30</sub>H<sub>36</sub>Li<sub>2</sub>**  
m-[C<sub>6</sub>H<sub>5</sub>CLi(CH<sub>2</sub>C<sub>4</sub>H<sub>9</sub>-s)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>  
Formation: 5.5.2.3.4
- C<sub>30</sub>H<sub>40</sub>Sn**  
[C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>CCH<sub>2</sub>]<sub>3</sub>SnH  
Reaction with R<sub>2</sub>Hg: 5.7.5.2.3
- C<sub>30</sub>H<sub>54</sub>O<sub>2</sub>Sn**  
2,4,6-(i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>C(O)OCH(CH<sub>3</sub>)Sn(n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>30</sub>H<sub>66</sub>CdSn<sub>2</sub>**  
[(Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Cd  
Formation: 5.7.5.2.2
- C<sub>30</sub>H<sub>66</sub>HgSn<sub>2</sub>**  
[(Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
Formation: 5.7.5.2.3
- C<sub>31</sub>H<sub>25</sub>NaZn**  
Na[Zn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]  
Formation and structure: 5.7.2.4.3
- C<sub>31</sub>H<sub>26</sub>AsLiPb**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCH(Li)As(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.1
- C<sub>31</sub>H<sub>26</sub>AsLiSn**  
(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH(Li)As(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
Formation: 5.5.2.3.2
- C<sub>32</sub>H<sub>30</sub>Hg**  
[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CCH<sub>2</sub>CCH<sub>3</sub>]<sub>2</sub>Hg  
Formation: 5.7.2.2.1
- C<sub>32</sub>H<sub>36</sub>O<sub>4</sub>Sn**  
(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>)<sub>4</sub>Sn  
Transmetallation: 5.5.2.3.1
- C<sub>32</sub>H<sub>40</sub>Br<sub>2</sub>Cu<sub>6</sub>N<sub>4</sub>**  
Cu<sub>2</sub>Br<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)<sub>4</sub>  
Reaction with RLi: 5.6.4.1
- C<sub>33</sub>H<sub>28</sub>Sn**  
(E)-C<sub>6</sub>H<sub>5</sub>C[Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]=CH(C<sub>6</sub>H<sub>5</sub>)CH<sub>3</sub>  
Transmetallation: 5.5.2.3.1
- C<sub>33</sub>H<sub>36</sub>Ag<sub>3</sub>N<sub>3</sub>O<sub>3</sub>**  
[p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>C=NC(OC<sub>2</sub>H<sub>5</sub>)Ag]<sub>3</sub>  
Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>34</sub>H<sub>26</sub>Ge**  
PhC(Ph)C(Ph)C(Ph)CGePhH  
Reaction with RLi: 5.5.5.4
- C<sub>34</sub>H<sub>30</sub>Ge<sub>2</sub>Hg**  
[CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)(1-C<sub>10</sub>H<sub>7</sub>)Ge]<sub>2</sub>Hg  
Formation: 5.7.4.2
- C<sub>34</sub>H<sub>30</sub>HgSi<sub>2</sub>**  
[CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)(1-C<sub>10</sub>H<sub>7</sub>)Si]<sub>2</sub>Hg  
Formation: 5.7.3.3
- C<sub>34</sub>H<sub>40</sub>Ag<sub>4</sub>Au<sub>2</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>**  
[Ag<sub>2</sub>Au(O<sub>3</sub>SCF<sub>3</sub>)(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)<sub>2</sub>]<sub>2</sub>  
Formation: 5.6.4, 5.6.4.1
- C<sub>34</sub>H<sub>62</sub>Hg**  
[CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>C≡C]<sub>2</sub>Hg  
Reaction with Li metal: 5.5.2.2.2
- C<sub>35</sub>H<sub>33</sub>NSn**  
(E)-o-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C[Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]=C\*  
(C<sub>6</sub>H<sub>5</sub>)CH<sub>3</sub>  
Transmetallation: 5.5.2.3.1

- C<sub>36</sub>CdF<sub>30</sub>Ge<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Cd  
 Formation: 5.7.4.2  
 Reaction with Hg metal: 5.7.4.2
- C<sub>36</sub>CdF<sub>30</sub>Sn<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>Cd  
 Formation: 5.7.5.2.2
- C<sub>36</sub>Cs**  
 CsC<sub>36</sub>  
 Formation: 5.5.3.1.2
- C<sub>36</sub>F<sub>30</sub>GeHgSn**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>SnHgGe(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>  
 Formation: 5.7.5.3
- C<sub>36</sub>F<sub>30</sub>Ge<sub>2</sub>**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>GeGe(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>  
 Reaction with RHgX: 5.7.4.5
- C<sub>36</sub>F<sub>30</sub>Ge<sub>2</sub>Hg**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Hg  
 Formation: 5.7.4.2, 5.7.4.4, 5.7.4.6  
 Reaction with HgX<sub>2</sub>: 5.7.4.6  
 Reaction with Pr metal: 5.7.4  
 Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4.6
- C<sub>36</sub>F<sub>30</sub>Ge<sub>2</sub>Zn**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Zn  
 Formation: 5.7.4.2  
 Reaction with Hg metal: 5.7.4.2
- C<sub>36</sub>F<sub>30</sub>HgSn<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
 Formation: 5.7.5.2.3, 5.7.5.3
- C<sub>36</sub>H<sub>24</sub>Hg<sub>2</sub>**  
 (2,2'-o-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg<sub>2</sub>  
 Reaction with Li metal: 5.5.2.2.2
- C<sub>36</sub>H<sub>24</sub>Hg<sub>3</sub>**  
 [o-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Hg-o]<sub>3</sub>  
 Formation: 5.7.2.3.1
- C<sub>36</sub>H<sub>24</sub>Hg<sub>6</sub>**  
 (o-C<sub>6</sub>H<sub>4</sub>Hg)<sub>6</sub>  
 Reaction with Li metal: 5.5.2.2.2
- C<sub>36</sub>H<sub>27</sub>Sb**  
 [p-(C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Sb  
 Transmetalation: 5.5.2.3.1
- C<sub>36</sub>H<sub>30</sub>AuCl<sub>3</sub>P<sub>2</sub>Sn**  
 (Ph<sub>3</sub>P)<sub>2</sub>AuSnCl<sub>3</sub>  
 Formation: 5.6.5.4
- C<sub>36</sub>H<sub>30</sub>AuGeP**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeAu·PPh<sub>3</sub>  
 Formation: 5.6.5.1  
 Reaction with RLi: 5.6.5.1  
 Reaction with R<sub>3</sub>GeLi: 5.6.5.1  
 Reaction with SnX<sub>4</sub>: 5.6.5.4
- C<sub>36</sub>H<sub>30</sub>AuGe<sub>2</sub>Li**  
 Li[(Ph<sub>3</sub>Ge)<sub>2</sub>Au]  
 Formation: 5.6.5.1
- C<sub>36</sub>H<sub>30</sub>AuPSi**  
 SiAu·PPh<sub>3</sub>  
 Formation: 5.6.5.1
- C<sub>36</sub>H<sub>30</sub>Au<sub>2</sub>I<sub>2</sub>P<sub>2</sub>Sn**  
 (Ph<sub>3</sub>P)<sub>2</sub>Au<sub>2</sub>SnI<sub>2</sub>  
 Formation: 5.6.5.2
- C<sub>36</sub>H<sub>30</sub>CdGe<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Cd  
 Reaction with (Ph<sub>3</sub>P)<sub>3</sub>Pd: 5.7.4
- C<sub>36</sub>H<sub>30</sub>CdSn<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>Cd  
 Formation of complex: 5.7.5.2.2
- C<sub>36</sub>H<sub>30</sub>Cu<sub>4</sub>Mg**  
 Cu<sub>4</sub>Mg(C<sub>6</sub>H<sub>5</sub>)<sub>6</sub>  
 Formation: 5.6.4.1
- C<sub>36</sub>H<sub>30</sub>F<sub>2</sub>Ge<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>GeF<sub>2</sub>  
 Formation: 5.7.4.8
- C<sub>36</sub>H<sub>30</sub>F<sub>2</sub>Ge<sub>3</sub>Hg**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeGeF<sub>2</sub>HgGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.7.4.8
- C<sub>36</sub>H<sub>30</sub>Ge<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with PhLi: 5.5.5.2.2  
 Reaction with Li, Na, Na-K: 5.5.5.2.2  
 Reaction with Li, Na, Na-K, K or Cs metal: 5.5.5.2.1  
 Reaction with [C<sub>10</sub>H<sub>8</sub>]<sup>-</sup>Na<sup>+</sup>: 5.5.5.2.1  
 Reaction with Na metal: 5.5.5.2.1
- C<sub>36</sub>H<sub>30</sub>Ge<sub>2</sub>Hg**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Hg  
 Reaction with (Ph<sub>3</sub>P)<sub>3</sub>Pd: 5.7.4  
 Reaction with RGeX: 5.7.4.8  
 Reaction with Li metal: 5.5.5.6
- C<sub>36</sub>H<sub>30</sub>Ge<sub>2</sub>Zn**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Zn  
 Formation: 5.7.4.1
- C<sub>36</sub>H<sub>30</sub>HgSi<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]<sub>2</sub>Hg  
 Formation: 5.7.3.2, 5.7.3.3
- C<sub>36</sub>H<sub>30</sub>HgSn<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
 Formation: 5.7.5, 5.7.5.2.3  
 Reaction with Pt(PPh<sub>3</sub>)<sub>3</sub>: 5.7.5
- C<sub>36</sub>H<sub>30</sub>Pb<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbPb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.5.7.4  
 Reaction with Hg(OAc)<sub>2</sub>: 5.7.6.2  
 Reaction with HgX<sub>2</sub>: 5.7.6.2  
 Reaction with group-IA metals: 5.5.7.2.1  
 Reaction with PhLi: 5.5.7.2.2  
 Reaction with RHgX: 5.7.6.2

- C<sub>36</sub>H<sub>30</sub>Si<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiSi(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.5.4.7, 5.6.5.1, 5.7.3.2  
 Reaction with RLi: 5.5.4.2.2  
 Reaction with Rb, Cs or Li metal: 5.5.4.2.1  
 Reaction with K metal: 5.7.3.1  
 Reaction with Na or K metal: 5.5.4.2.1
- C<sub>36</sub>H<sub>30</sub>Sn<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnSn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.7.5.1.1  
 Reaction with PhLi: 5.5.6  
 Reaction with Li: 5.5.6.2.1  
 Reaction with KH: 5.5.6  
 Reaction with Na naphthalene: 5.5.6.2.2
- C<sub>36</sub>H<sub>30</sub>Sn<sub>2</sub>Zn**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>Zn  
 Formation: 5.7.5  
 Formation of complex: 5.7.5.2.1
- C<sub>36</sub>H<sub>34</sub>BCu**  
 CuBH<sub>4</sub> · 2PPh<sub>3</sub>  
 Reaction with HC≡CPh: 5.6.4.3
- C<sub>36</sub>H<sub>36</sub>N<sub>2</sub>Sn<sub>2</sub>Zn**  
 Zn[Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> · 2NH<sub>3</sub>  
 Formation: 5.7.3.1
- C<sub>36</sub>H<sub>40</sub>Br<sub>2</sub>Cu<sub>4</sub>N<sub>2</sub>**  
 Cu<sub>4</sub>Br<sub>2</sub>[C(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)=CMe(C<sub>6</sub>H<sub>4</sub>-Me-4)]<sub>2</sub>  
 Formation: 5.6.4, 5.6.4.3
- C<sub>36</sub>H<sub>40</sub>Li<sub>2</sub>N<sub>4</sub> · Au<sub>2</sub>**
- C<sub>36</sub>H<sub>42</sub>Hg**  
 [(CH<sub>3</sub>)<sub>3</sub>CC(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>Hg  
 Reaction with Na metal: 5.5.3.2.3
- C<sub>36</sub>H<sub>48</sub>Ag<sub>2</sub>Li<sub>2</sub>N<sub>4</sub>**  
 [AgLi(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)]<sub>2</sub>  
 Formation: 5.6.4, 5.6.4.1
- C<sub>36</sub>H<sub>48</sub>Au<sub>2</sub>Li<sub>2</sub>N<sub>4</sub>**  
 [AuLi(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)]<sub>2</sub>  
 Formation: 5.6.4, 5.6.4.1
- C<sub>36</sub>H<sub>48</sub>Cu<sub>2</sub>Li<sub>2</sub>N<sub>4</sub>**  
 [CuLi(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-2)]<sub>2</sub>  
 Formation: 5.6.4.1
- C<sub>36</sub>H<sub>48</sub>Cu<sub>4</sub>N<sub>4</sub>**  
 [CuC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>-2]<sub>4</sub>  
 Formation: 5.6.4, 5.6.4.1  
 Interaggregate Exchange: 5.6.4.1  
 Reaction with CNR: 5.6.4.4
- C<sub>36</sub>H<sub>66</sub>Pb<sub>2</sub>**  
 (C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>PbPb(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>  
 Reaction with group-IA: 5.5.7.2.1  
 Reaction with Na metal: 5.5.7.3
- C<sub>36</sub>H<sub>75</sub>B**  
 (n-C<sub>12</sub>H<sub>25</sub>)<sub>3</sub>B  
 Formation: 5.7.2.3.1
- Reaction with HgX<sub>2</sub>: 5.7.2.3.1
- C<sub>36</sub>H<sub>99</sub>Si<sub>3</sub>Tl**  
 [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>Si]<sub>3</sub>Tl  
 Reaction with Hg metal: 5.7.3.4
- C<sub>36</sub>K**  
 KC<sub>36</sub>  
 Formation: 5.5.3.1.2
- C<sub>36</sub>Rb**  
 RbC<sub>36</sub>  
 Formation: 5.5.3.1.2
- C<sub>37</sub>H<sub>30</sub>Cl<sub>2</sub>GePb**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb][(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]CCl<sub>2</sub>  
 Reaction with RLi: 5.5.2.3.1
- C<sub>37</sub>H<sub>30</sub>Cl<sub>2</sub>PbSi**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb][(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Si]CCl<sub>2</sub>  
 Reaction with RLi: 5.5.2.3.1
- C<sub>37</sub>H<sub>30</sub>Cl<sub>2</sub>PbSn**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb][(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]CCl<sub>2</sub>  
 Reaction with RLi: 5.5.2.3.1
- C<sub>37</sub>H<sub>30</sub>Cl<sub>2</sub>Pb<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>2</sub>CCl<sub>2</sub>  
 Transmetalation: 5.5.2.3.1
- C<sub>37</sub>H<sub>30</sub>Ge**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeC(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with Na-K: 5.5.5.5
- C<sub>37</sub>H<sub>30</sub>Si**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiC(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with Na-K: 5.5.4.5
- C<sub>37</sub>H<sub>31</sub>As<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>As]<sub>3</sub>CH  
 Reaction with RLi: 5.5.2.3.1
- C<sub>37</sub>H<sub>31</sub>GeLiPb**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCHLiGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.5.2.3.1
- C<sub>37</sub>H<sub>31</sub>LiPb<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>2</sub>CHLi  
 Formation: 5.5.2.3.1, 5.5.2.3.2
- C<sub>37</sub>H<sub>31</sub>LiSn<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>2</sub>CHLi  
 Formation: 5.5.2.3.2
- C<sub>37</sub>H<sub>31</sub>Sb<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Sb]<sub>3</sub>CH  
 Reaction with RLi: 5.5.2.3.1
- C<sub>37</sub>H<sub>32</sub>GePb**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PbCH<sub>2</sub>Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Transmetalation: 5.5.2.3.1
- C<sub>37</sub>H<sub>32</sub>Pb<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>2</sub>CH<sub>2</sub>  
 Transmetalation: 5.5.2.3.1
- C<sub>37</sub>H<sub>33</sub>Cu**  
 CH<sub>3</sub>Cu · 2PPh<sub>3</sub>  
 Reaction with RCN: 5.6.4.3

- Reaction with RH: 5.6.4.3  
**C<sub>37</sub>H<sub>33</sub>CuP<sub>2</sub>**  
 CH<sub>3</sub>Cu · 2PPh<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>37</sub>H<sub>37</sub>NSn**  
 (E)-o-(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C[Sn\*  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]=C[C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-p]CH<sub>3</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>38</sub>H<sub>5</sub>BiF<sub>30</sub>Ge<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>BiC<sub>2</sub>H<sub>5</sub>  
 Reaction with Hg metal: 5.7.4.4
- C<sub>38</sub>H<sub>30</sub>O<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C(OC<sub>6</sub>H<sub>5</sub>)C(OC<sub>6</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
 Reaction with Li metal: 5.5.2.2.5
- C<sub>38</sub>H<sub>32</sub>CuNP<sub>2</sub>**  
 NCCH<sub>2</sub>Cu · 2PPh<sub>3</sub>  
 Formation: 5.6.4.3
- C<sub>38</sub>H<sub>32</sub>Sn<sub>2</sub>**  
 (E)-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnCH=CHSn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>38</sub>H<sub>35</sub>CuP<sub>2</sub>**  
 C<sub>2</sub>H<sub>5</sub>Cu · 2PPh<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>38</sub>H<sub>36</sub>Si<sub>3</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiSi(CH<sub>3</sub>)<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Reaction with Li metal: 5.5.4.2.1
- C<sub>39</sub>H<sub>30</sub>Au<sub>2</sub>N<sub>2</sub>**  
 [Au(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>C(CN)<sub>2</sub>  
 Formation: 5.6.4.3
- C<sub>39</sub>H<sub>30</sub>CoLiSn**  
 h<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Co[C(SnPh<sub>3</sub>)CPhCLiCPh]  
 Formation: 5.5.2.3.1
- C<sub>39</sub>H<sub>31</sub>CuN<sub>2</sub>**  
 Cu[CH(CN)<sub>2</sub>]<sub>2</sub> · 2PPh<sub>3</sub>  
 Formation: 5.6.4.3
- C<sub>39</sub>H<sub>34</sub>CuN**  
 Cu[CH(CH<sub>3</sub>)CN]<sub>2</sub> · 2PPh<sub>3</sub>  
 Formation: 5.6.4.3
- C<sub>39</sub>H<sub>37</sub>CuP<sub>2</sub>**  
 n-C<sub>3</sub>H<sub>7</sub>Cu · 2PPh<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>40</sub>H<sub>30</sub>Au<sub>2</sub>F<sub>6</sub>P<sub>2</sub>**  
 Ph<sub>3</sub>PAuC(CF<sub>3</sub>)=C(CF<sub>3</sub>)AuPPh<sub>3</sub>  
 Formation: 5.6.4.5
- C<sub>40</sub>H<sub>35</sub>CuO<sub>2</sub>P<sub>2</sub>**  
 Cu[CH=C(H)OC(=O)CH<sub>3</sub>]<sub>2</sub> · 2PPh<sub>3</sub>  
 Formation: 5.6.4.3
- C<sub>40</sub>H<sub>36</sub>Li<sub>2</sub>Si<sub>2</sub>**  
 Ph<sub>3</sub>SiCH(Li)CH<sub>2</sub>CH<sub>2</sub>CH(Li)SiPh<sub>3</sub>  
 Formation: 5.5.2.2.3
- C<sub>40</sub>H<sub>39</sub>CuP<sub>2</sub>**  
 i-C<sub>4</sub>H<sub>9</sub>Cu · 2PPh<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>40</sub>H<sub>40</sub>Pb<sub>2</sub>Si**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>2</sub>CHSi(CH<sub>3</sub>)<sub>3</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>40</sub>H<sub>56</sub>Cu<sub>4</sub>N<sub>4</sub>**  
 [CuC<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>NMe<sub>2</sub>-2-CH<sub>3</sub>-5]<sub>4</sub>  
 Reaction with CuI: 5.6.4.1
- C<sub>42</sub>H<sub>30</sub>AuF<sub>5</sub>P**  
 C<sub>6</sub>F<sub>5</sub>Au · PPh<sub>3</sub>  
 Formation: 5.6.4.5
- C<sub>42</sub>H<sub>35</sub>ClGe<sub>3</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeGe(C<sub>6</sub>H<sub>5</sub>)ClGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.7.4.8
- C<sub>42</sub>H<sub>35</sub>ClGe<sub>3</sub>Hg**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeGe(C<sub>6</sub>H<sub>5</sub>)ClHgGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Formation: 5.7.4.8
- C<sub>42</sub>H<sub>35</sub>CuN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>**  
 Cu[CC<sub>6</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> · 2(PPh<sub>3</sub>)<sub>2</sub>  
 Formation: 5.6.4.3
- C<sub>42</sub>H<sub>42</sub>Pb<sub>2</sub>**  
 (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PbPb(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>  
 Reaction with group-IA: 5.5.7.2.1
- C<sub>42</sub>H<sub>42</sub>Si<sub>2</sub>**  
 (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SiSi(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>3</sub>  
 Reaction with K metal: 5.5.4.2.1
- C<sub>42</sub>H<sub>44</sub>Ge<sub>2</sub>O<sub>3</sub>Zn**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Zn · O(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>  
 Formation: 5.7.4.2
- C<sub>43</sub>H<sub>37</sub>AuBF<sub>4</sub>P<sub>2</sub>**  
 [[Au(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4]BF<sub>4</sub>  
 Formation: 5.6.4.3
- C<sub>44</sub>H<sub>20</sub>F<sub>30</sub>Ge<sub>2</sub>O<sub>2</sub>Zn**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Zn · 2 O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>  
 Formation: 5.7.4.2
- C<sub>44</sub>H<sub>36</sub>AuBrF<sub>15</sub>N**  
 [n-C<sub>4</sub>H<sub>9</sub>N][AuBr(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]  
 Formation: 5.6.4.1
- C<sub>44</sub>H<sub>39</sub>AuGeP<sub>2</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeAuP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
 Formation: 5.6.5.1
- C<sub>48</sub>Cs**  
 CsC<sub>48</sub>  
 Formation: 5.5.3.1.2
- C<sub>48</sub>H<sub>40</sub>Ge<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Ge]<sub>4</sub>  
 Formation: 5.7.4.2  
 Reaction with [C<sub>10</sub>H<sub>8</sub>]<sup>-</sup>Na<sup>+</sup>: 5.5.5.2.1  
 Reaction with Na metal: 5.5.5.2.2
- C<sub>48</sub>H<sub>40</sub>Li<sub>2</sub>Si<sub>4</sub>**  
 Li[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>4</sub>Li  
 Formation: 5.5.4.2.1
- C<sub>48</sub>H<sub>40</sub>Na<sub>2</sub>Si<sub>4</sub>**  
 Na[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>4</sub>Na  
 Formation: 5.5.4.2.1

- C<sub>48</sub>H<sub>40</sub>Si<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>4</sub>  
 Reaction with RLi: 5.5.4.2.2  
 Reaction with Li metal: 5.5.4.2.1  
 Reaction with Na metal: 5.5.4.2.1
- C<sub>48</sub>H<sub>108</sub>Cu<sub>4</sub>I<sub>4</sub>P<sub>4</sub>**  
 [CuI(PBu<sub>3</sub>)<sub>4</sub>]<sub>4</sub>  
 Reaction with RCu: 5.6.4.1
- C<sub>48</sub>K**  
 KC<sub>48</sub>  
 Formation: 5.5.3.1.2
- C<sub>48</sub>Rb**  
 RbC<sub>48</sub>  
 Formation: 5.5.3.1.2
- C<sub>49</sub>H<sub>41</sub>AsPb<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>2</sub>CHAs(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>49</sub>H<sub>43</sub>LiSi<sub>4</sub>**  
 CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>2</sub>Si(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Li  
 Formation: 5.5.4.2.2
- C<sub>50</sub>H<sub>54</sub>Cu<sub>6</sub>N<sub>4</sub>**  
 [Cu<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)<sub>2</sub>](C≡CCC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>  
 Formation: 5.6.4.3  
 Cu<sub>6</sub>(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>  
 Formation: 5.6.4.1
- C<sub>50</sub>H<sub>72</sub>Cu<sub>2</sub>P<sub>6</sub>**  
 [Cu(I)CH<sub>3</sub>]<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>52</sub>H<sub>76</sub>Cu<sub>2</sub>P<sub>6</sub>**  
 [Cu(I)C<sub>2</sub>H<sub>5</sub>]<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>54</sub>H<sub>48</sub>AgClP<sub>3</sub>**  
 (Ph<sub>3</sub>P)<sub>3</sub>AgCl  
 Reaction with SnCl<sub>2</sub>: 5.6.5.2
- C<sub>54</sub>H<sub>48</sub>AgCl<sub>3</sub>P<sub>3</sub>Sn**  
 (Ph<sub>3</sub>P)<sub>3</sub>AgSnCl<sub>3</sub>  
 Formation: 5.6.5.2
- C<sub>54</sub>H<sub>48</sub>AuClP<sub>3</sub>**  
 (Ph<sub>3</sub>P)<sub>3</sub>AuCl  
 Reaction with SnCl<sub>2</sub>: 5.6.5.2
- C<sub>54</sub>H<sub>48</sub>AuCl<sub>3</sub>P<sub>3</sub>Sn**  
 (Ph<sub>3</sub>P)<sub>3</sub>AuSnCl<sub>3</sub>  
 Formation: 5.6.5.2
- C<sub>54</sub>H<sub>48</sub>Au<sub>3</sub>BF<sub>4</sub>OP**  
 [[Au(PPh<sub>3</sub>)<sub>3</sub>O]<sub>3</sub>BF<sub>4</sub>]  
 Reaction with C—H: 5.6.4.3
- C<sub>54</sub>H<sub>48</sub>ClCuP<sub>3</sub>**  
 (Ph<sub>3</sub>P)<sub>3</sub>CuCl  
 Reaction with SnCl<sub>2</sub>: 5.6.5.2
- C<sub>54</sub>H<sub>48</sub>Cl<sub>3</sub>CuP<sub>3</sub>Sn**  
 (Ph<sub>3</sub>P)<sub>3</sub>CuSnCl<sub>3</sub>  
 Formation: 5.6.5.2
- C<sub>54</sub>H<sub>48</sub>Ge<sub>3</sub>LiSi**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>SiLi  
 Formation: 5.5.4.4
- C<sub>54</sub>H<sub>48</sub>Ge<sub>4</sub>Li**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>GeLi  
 Formation: 5.5.5.4, 5.5.5.7
- C<sub>54</sub>H<sub>48</sub>LiSn<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>3</sub>SnLi  
 Formation: 5.5.6.6
- C<sub>54</sub>H<sub>48</sub>P<sub>3</sub>Pd**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>Pd  
 Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Cd: 5.7.4  
 Reaction with (R<sub>3</sub>Ge)<sub>2</sub>Hg: 5.7.4
- C<sub>54</sub>H<sub>46</sub>Ge<sub>3</sub>Si**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>SiH  
 Reaction with Li metal: 5.5.4.4
- C<sub>54</sub>H<sub>46</sub>Ge<sub>4</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>GeH  
 Formation: 5.5.5.7  
 Reaction with RLi: 5.5.5.4
- C<sub>54</sub>H<sub>80</sub>Cu<sub>2</sub>P<sub>6</sub>**  
 [Cu(I)n-C<sub>3</sub>H<sub>7</sub>](Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>54</sub>H<sub>84</sub>Cu<sub>2</sub>P<sub>6</sub>**  
 [Cu(I)-C<sub>4</sub>H<sub>9</sub>](Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>  
 Formation: 5.6.4.1
- C<sub>55</sub>H<sub>45</sub>LiS<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>S]<sub>3</sub>CLi  
 Formation: 5.5.2.3.1
- C<sub>55</sub>H<sub>46</sub>GePb<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>2</sub>CHGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>  
 Transmetallation: 5.5.2.3.1
- C<sub>55</sub>H<sub>46</sub>Pb<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Pb]<sub>3</sub>CH  
 Reaction with RLi: 5.5.2.3.1  
 Transmetallation: 5.5.2.3.1
- C<sub>55</sub>H<sub>46</sub>Sn<sub>3</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>3</sub>CH  
 Reaction with RLi: 5.5.2.3.1
- C<sub>57</sub>H<sub>45</sub>CoSn<sub>2</sub>**  

$$\text{h}^5\text{-C}_5\text{H}_5\text{Co}[\overline{\text{C}(\text{Ph}_3\text{Sn})=\text{CPh}-\text{C}(\text{Sn}^*\text{Ph}_3)=\text{CPh}}]$$
  
 Reaction with RLi: 5.5.2.3.1
- C<sub>60</sub>Cs**  
 CsC<sub>60</sub>  
 Formation: 5.5.3.1.2
- C<sub>60</sub>H<sub>50</sub>Ge<sub>5</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Ge]<sub>5</sub>  
 Formation: 5.7.4.2
- C<sub>60</sub>H<sub>50</sub>Li<sub>2</sub>Si<sub>5</sub>**  
 Li[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>5</sub>Li  
 Formation: 5.5.4.2.1

- C<sub>60</sub>H<sub>50</sub>P<sub>2</sub>PbPt**  
 cis-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtC<sub>6</sub>H<sub>5</sub>[Pb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]  
 Formation: 5.5.7.6
- C<sub>60</sub>H<sub>50</sub>Si<sub>5</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>5</sub>  
 Reaction with Ph<sub>3</sub>SiLi: 5.5.4.2.2
- C<sub>60</sub>H<sub>68</sub>HgSn<sub>2</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>(Me)<sub>2</sub>CCH<sub>2</sub>)<sub>3</sub>Sn]<sub>2</sub>Hg  
 Formation: 5.7.5.2.3
- C<sub>60</sub>K**  
 KC<sub>60</sub>  
 Formation: 5.5.3.1.2
- C<sub>60</sub>Rb**  
 RbC<sub>60</sub>  
 Formation: 5.5.3.1.2
- C<sub>64</sub>Na**  
 NaC<sub>64</sub>  
 Formation: 5.5.3.1.1
- C<sub>72</sub>H<sub>30</sub>CdF<sub>30</sub>Ge<sub>2</sub>P<sub>2</sub>**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Cd · 2 PPh<sub>3</sub>  
 Formation: 5.7.4.2
- C<sub>72</sub>H<sub>60</sub>AgGe**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeAg · 3 PPh<sub>3</sub>  
 Formation: 5.6.5.1
- C<sub>72</sub>H<sub>60</sub>Ag<sub>4</sub>I<sub>4</sub>P<sub>4</sub>**  
 (Ph<sub>3</sub>PAgI)<sub>4</sub>  
 Reaction with R<sub>3</sub>GeLi: 5.6.5.1
- C<sub>72</sub>H<sub>60</sub>Au<sub>4</sub>Cl<sub>3</sub>P<sub>4</sub>Sn**  
 (Ph<sub>3</sub>P)<sub>4</sub>Au<sub>4</sub>SnCl<sub>3</sub>  
 Formation: 5.6.5.2
- C<sub>72</sub>H<sub>60</sub>CdGe<sub>2</sub>P<sub>2</sub>Pd**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pd[Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>][CdGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]  
 Formation: 5.7.4
- C<sub>72</sub>H<sub>60</sub>CuGeP<sub>3</sub>**  
 (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>GeCu(PPh<sub>3</sub>)<sub>3</sub>  
 Formation: 5.6.5.1
- C<sub>72</sub>H<sub>60</sub>Cu<sub>4</sub>I<sub>4</sub>P<sub>4</sub>**  
 (Ph<sub>3</sub>PCuI)<sub>4</sub>  
 Reaction with R<sub>3</sub>GeLi: 5.6.5.1
- C<sub>72</sub>H<sub>60</sub>Ge<sub>2</sub>HgP<sub>2</sub>Pd**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pd[Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>][HgGe(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]  
 Formation: 5.7.4
- C<sub>72</sub>H<sub>60</sub>Li<sub>2</sub>Si<sub>6</sub>**  
 Li[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>6</sub>Li  
 Disproportionation: 5.5.4.2.1  
 Formation: 5.5.4.2.1
- C<sub>72</sub>H<sub>60</sub>P<sub>2</sub>Pb<sub>2</sub>Pt**  
 cis-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>Pt[Pb(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>  
 Reaction with PhLi: 5.5.7.6
- C<sub>72</sub>H<sub>60</sub>Si<sub>6</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si]<sub>6</sub>  
 Reaction with R<sub>3</sub>SiLi: 5.5.4.2.2
- Reaction with Li metal: 5.5.4.2.1
- C<sub>72</sub>H<sub>60</sub>Sn<sub>5</sub>**  
 [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>4</sub>Sn  
 Formation: 5.5.6.6
- C<sub>78</sub>H<sub>63</sub>Cu<sub>3</sub>P<sub>6</sub>**  
 Cu<sub>3</sub>(Ph<sub>2</sub>PCHPPh<sub>2</sub>)<sub>3</sub>  
 Formation: 5.6.4.3
- C<sub>78</sub>H<sub>36</sub>F<sub>30</sub>HgP<sub>2</sub>PtSn<sub>2</sub>**  
 (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>SnHgPt[PPh<sub>3</sub>]<sub>2</sub>Sn(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> · C<sub>6</sub>H<sub>6</sub>  
 Formation: 5.7.5
- C<sub>90</sub>F<sub>75</sub>Ge<sub>5</sub>HgPr**  
 [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>2</sub>Pr[[C(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ge]<sub>3</sub>Hg]  
 Formation: 5.7.4
- C<sub>104</sub>H<sub>80</sub>Cu**  
 [CuC≡CC<sub>6</sub>H<sub>5</sub> · 2 PPh<sub>3</sub>]<sub>4</sub>  
 Formation: 5.6.4.3
- CaCl<sub>2</sub>**  
 CaCl<sub>2</sub>  
 Electrolyte: 5.5.7.1.3
- CaZn\* C<sub>8</sub>H<sub>20</sub>**
- Cd**  
 Cd  
 Reaction with R<sub>2</sub>Hg: 5.7.2.2.2  
 Reaction with R<sub>3</sub>SnX: 5.7.5.1.2  
 Reaction with RX: 5.7.2.2.1
- Cd\*Br<sub>2</sub>**
- Cd\*C<sub>2</sub>H<sub>5</sub>Br**
- Cd\*C<sub>2</sub>H<sub>6</sub>**
- Cd\*C<sub>3</sub>H<sub>6</sub>**
- Cd\*C<sub>4</sub>H<sub>3</sub>Br**
- Cd\*C<sub>4</sub>H<sub>9</sub>Br**
- Cd\*C<sub>4</sub>H<sub>10</sub>**
- Cd\*C<sub>6</sub>H<sub>5</sub>Br**
- Cd\*C<sub>6</sub>H<sub>14</sub>**
- Cd\*C<sub>8</sub>H<sub>14</sub>**
- Cd\*C<sub>10</sub>H<sub>10</sub>**
- Cd\*C<sub>10</sub>H<sub>22</sub>**
- Cd\*C<sub>12</sub>H<sub>10</sub>**
- Cd\*C<sub>12</sub>H<sub>22</sub>**
- Cd\*C<sub>14</sub>H<sub>14</sub>**
- Cd\*C<sub>16</sub>H<sub>10</sub>**
- CdCl\*CH<sub>3</sub>**
- CdCl\*C<sub>2</sub>H<sub>5</sub>**
- CdCl\*C<sub>3</sub>H<sub>7</sub>**
- CdCl\*C<sub>4</sub>H<sub>9</sub>**
- CdClSn\*C<sub>18</sub>H<sub>15</sub>**
- CdCl<sub>2</sub>**  
 CdCl<sub>2</sub>  
 Electrolyte: 5.7.6.1.3  
 Reaction with RLi: 5.7.2.3.1  
 Reaction with R<sub>2</sub>Cd: 5.7.2.3.2  
 Reaction with Zn metal: 5.7.6.1.2

- $\text{CdCl}_2 \cdot \text{C}_{12}\text{H}_8$   
 $\text{CdF}_2\text{O}_3\text{P} \cdot \text{C}_5\text{H}_{10}\text{Br}$   
 $\text{CdF}_4\text{O}_2\text{P}_2 \cdot \text{C}_{10}\text{H}_{20}$   
 $\text{CdF}_5 \cdot \text{C}_6\text{Br}$   
 $\text{CdF}_{10} \cdot \text{C}_{12}$   
 $\text{CdF}_{30}\text{Ge}_2 \cdot \text{C}_{36}$   
 $\text{CdF}_{30}\text{Ge}_2\text{P}_2 \cdot \text{C}_{72}\text{H}_{30}$   
 $\text{CdF}_{30}\text{Sn}_2 \cdot \text{C}_{36}$   
 $\text{CdGe}_2 \cdot \text{C}_{12}\text{H}_{30}$   
 $\text{CdGe}_2 \cdot \text{C}_{36}\text{H}_{30}$   
 $\text{CdGe}_2\text{P}_2\text{Pd} \cdot \text{C}_{72}\text{H}_{60}$   
 $\text{CdI} \cdot \text{CH}_3$   
 $\text{CdI} \cdot \text{C}_2\text{H}_5$   
 $\text{CdI} \cdot \text{C}_6\text{H}_5$   
**CdI<sub>2</sub>**  
 $\text{CdI}_2$   
 Reaction with  $\text{R}_2\text{Cd}$ : 5.7.2.3.2  
 Reaction with  $\text{CH}_2\text{N}_2$ : 5.7.2.3.5  
 $\text{CdI}_2 \cdot \text{C}_2\text{H}_4$   
 $\text{CdLi} \cdot \text{C}_{18}\text{H}_{15}$   
 $\text{CdN}_2\text{S}_2 \cdot \text{C}_2$   
 $\text{CdN}_2\text{Si}_4 \cdot \text{C}_{12}\text{H}_{36}$   
 $\text{CdN}_4\text{O}_4 \cdot \text{C}_8\text{H}_{10}$   
**CdO**  
 $\text{CdO}$   
 Reaction with 1,3-diketones: 5.7.2.3.4  
 $\text{CdO}_6 \cdot \text{C}_{12}\text{H}_{18}$   
 $\text{CdSi}_2 \cdot \text{C}_8\text{H}_{22}$   
 $\text{CdSi}_2 \cdot \text{C}_{12}\text{H}_{30}$   
 $\text{CdSi}_2 \cdot \text{C}_{24}\text{H}_{54}$   
 $\text{CdSi}_4 \cdot \text{C}_{14}\text{H}_{38}$   
 $\text{CdSi}_6 \cdot \text{C}_{20}\text{H}_{54}$   
 $\text{CdSi}_6\text{Sn}_2 \cdot \text{C}_{24}\text{H}_{66}$   
 $\text{CdSn}_2 \cdot \text{C}_{30}\text{H}_{66}$   
 $\text{CdSn}_2 \cdot \text{C}_{36}\text{H}_{30}$   
 $\text{Cl} \cdot \text{CH}_3\text{Cd}$   
 $\text{Cl} \cdot \text{C}_2\text{H}_5\text{Cd}$   
 $\text{Cl} \cdot \text{C}_3\text{H}_7\text{Cd}$   
 $\text{Cl} \cdot \text{C}_4\text{H}_9\text{Cd}$   
 $\text{Cl} \cdot \text{C}_4\text{H}_{10}\text{Al}$   
 $\text{Cl} \cdot \text{C}_5\text{H}_{11}$   
 $\text{Cl} \cdot \text{C}_6\text{H}_5$   
 $\text{Cl} \cdot \text{C}_8\text{H}_9$   
 $\text{Cl} \cdot \text{C}_9\text{H}_{11}$   
 $\text{Cl} \cdot \text{C}_{18}\text{H}_{21}$   
 $\text{Cl} \cdot \text{C}_{19}\text{H}_{15}$   
 $\text{Cl} \cdot \text{C}_{20}\text{H}_{17}$   
 $\text{Cl} \cdot \text{C}_{30}\text{H}_{25}\text{Au}$   
 $\text{ClCrHgO}_3 \cdot \text{C}_9\text{H}_5$   
 $\text{ClCu} \cdot \text{C}_6\text{H}_4$   
 $\text{ClCuP}_3 \cdot \text{C}_{54}\text{H}_{45}$   
 $\text{ClFHgO} \cdot \text{C}_{15}\text{H}_{12}$   
 $\text{ClFLiS} \cdot \text{C}_6\text{H}_9$   
 $\text{ClFLiSi} \cdot \text{C}_9\text{H}_{11}$   
 $\text{ClF}_3\text{Hg} \cdot \text{C}_7\text{H}_4$   
 $\text{ClF}_4\text{Hg} \cdot \text{C}_6\text{Br}$   
 $\text{ClF}_4\text{HgO} \cdot \text{C}_7\text{H}_3$   
 $\text{ClF}_5\text{Si} \cdot \text{C}_{18}\text{H}_{10}$   
 $\text{ClF}_5\text{Zn} \cdot \text{C}_6$   
 $\text{ClF}_9\text{Hg} \cdot \text{C}_4$   
 $\text{ClF}_{10}\text{P} \cdot \text{C}_{30}\text{H}_{15}\text{Au}$   
 $\text{ClF}_{15}\text{Ge} \cdot \text{C}_{18}$   
 $\text{ClFe} \cdot \text{C}_{10}\text{H}_8\text{Ag}$   
 $\text{ClFeHg} \cdot \text{C}_{10}\text{H}_9$   
 $\text{ClFeHg} \cdot \text{C}_{12}\text{H}_{11}$   
 $\text{ClFeHgMnO}_5 \cdot \text{C}_{15}\text{H}_9$   
 $\text{ClFeHgN} \cdot \text{C}_{13}\text{H}_{16}$   
 $\text{ClFeO}_2 \cdot \text{C}_{10}\text{H}_{10}\text{B}$   
 $\text{ClGe} \cdot \text{C}_3\text{H}_9$   
 $\text{ClGe} \cdot \text{C}_6\text{H}_5$   
 $\text{ClGe} \cdot \text{C}_6\text{H}_{15}$   
 $\text{ClGe} \cdot \text{C}_8\text{H}_{11}$   
 $\text{ClGe} \cdot \text{C}_{18}\text{H}_{15}$   
 $\text{ClGe}_3 \cdot \text{C}_{42}\text{H}_{35}$   
 $\text{ClGe}_3\text{Hg} \cdot \text{C}_{42}\text{H}_{35}$   
**ClH<sub>2</sub>HgN**  
 $\text{Hg}(\text{NH}_2)\text{Cl}$   
 Reaction with aliphatics: 5.7.2.3.4  
**ClH<sub>3</sub>Si**  
 $\text{H}_3\text{SiCl}$   
 Reaction with Na-Hg: 5.7.3.2  
 $\text{ClHg} \cdot \text{CD}_3$   
 $\text{ClHg} \cdot \text{CH}_3$   
 $\text{ClHg} \cdot \text{C}_2\text{H}_2\text{Br}$   
 $\text{ClHg} \cdot \text{C}_2\text{H}_3$   
 $\text{ClHg} \cdot \text{C}_2\text{H}_5$   
 $\text{ClHg} \cdot \text{C}_3\text{H}_3$   
 $\text{ClHg} \cdot \text{C}_3\text{H}_5$   
 $\text{ClHg} \cdot \text{C}_3\text{H}_7$   
 $\text{ClHg} \cdot \text{C}_4\text{H}_9$   
 $\text{ClHg} \cdot \text{C}_5\text{H}_4$   
 $\text{ClHg} \cdot \text{C}_5\text{H}_5$   
 $\text{ClHg} \cdot \text{C}_5\text{H}_7$   
 $\text{ClHg} \cdot \text{C}_6\text{H}_5$   
 $\text{ClHg} \cdot \text{C}_6\text{H}_{11}$   
 $\text{ClHg} \cdot \text{C}_6\text{H}_{11}\text{D}_2$   
 $\text{ClHg} \cdot \text{C}_6\text{H}_{13}$   
 $\text{ClHg} \cdot \text{C}_7\text{H}_7$   
 $\text{ClHg} \cdot \text{C}_8\text{H}_9$   
 $\text{ClHg} \cdot \text{C}_8\text{H}_{15}$   
 $\text{ClHg} \cdot \text{C}_9\text{H}_{13}$   
 $\text{ClHg} \cdot \text{C}_{10}\text{H}_{20}$   
 $\text{ClHg} \cdot \text{C}_{12}\text{H}_9$   
 $\text{ClHg} \cdot \text{C}_{12}\text{H}_{25}$

Cl:  $\text{gMnO}_3 \cdot \text{C}_8\text{H}_4$   
 ClF:  $\text{gN} \cdot \text{C}_2\text{H}_2$   
 ClHgN $\cdot \text{C}_6\text{H}_{14}$   
 ClHgN $\cdot \text{C}_8\text{H}_{16}$   
 ClHgN $\cdot \text{C}_9\text{H}_{12}$   
 ClHgNO $\cdot \text{C}_8\text{H}_{14}$   
 ClHgNO $\cdot \text{C}_9\text{H}_{16}$   
 ClHgNO $_2 \cdot \text{C}_6\text{H}_4$   
 ClHgNO $_2 \cdot \text{C}_6\text{H}_{10}$   
 ClHgNO $_2 \cdot \text{S} \cdot \text{C}_6\text{H}_6$   
 ClHgNO $_3 \cdot \text{C}_8\text{H}_6$   
 ClHgNO $_3 \cdot \text{C}_{14}\text{H}_{26}$   
 ClHgNO $_6 \cdot \text{C}_3\text{H}_6$   
 ClHgNS $\cdot \text{C}_3\text{H}_2$   
 ClHgN $_3 \cdot \text{C}_6\text{H}_{10}$   
 ClHgO $\cdot \text{C}_2\text{H}_5$   
 ClHgO $\cdot \text{C}_3\text{H}_5$   
 ClHgO $\cdot \text{C}_4\text{H}_3$   
 ClHgO $\cdot \text{C}_6\text{H}_9$   
 ClHgO $\cdot \text{C}_6\text{H}_{11}$   
 ClHgO $\cdot \text{C}_7\text{H}_{13}$   
 ClHgO $\cdot \text{C}_8\text{H}_9$   
 ClHgO $\cdot \text{C}_9\text{H}_7$   
 ClHgO $\cdot \text{C}_9\text{H}_9$   
 ClHgO $\cdot \text{C}_9\text{H}_{17}$   
 ClHgO $\cdot \text{C}_{11}\text{H}_{23}$   
 ClHgO $\cdot \text{C}_{16}\text{H}_{15}$   
 ClHgO $_2 \cdot \text{C}_2\text{H}_5$   
 ClHgO $_2 \cdot \text{C}_3\text{H}_7$   
 ClHgO $_2 \cdot \text{C}_3\text{H}_8\text{B}$   
 ClHgO $_2 \cdot \text{C}_5\text{H}_7$   
 ClHgO $_2 \cdot \text{C}_6\text{H}_7$   
 ClHgO $_2 \cdot \text{C}_6\text{H}_9$   
 ClHgO $_2 \cdot \text{C}_8\text{H}_{13}$   
 ClHgO $_2 \cdot \text{C}_9\text{H}_9$   
 ClHgO $_2 \cdot \text{C}_9\text{H}_{11}$   
 ClHgO $_2 \cdot \text{C}_{11}\text{H}_{19}$   
 ClHgO $_2 \cdot \text{C}_{16}\text{H}_{15}$   
 ClHgO $_2 \cdot \text{S} \cdot \text{C}_6\text{H}_{11}$   
 ClHgO $_2 \cdot \text{S} \cdot \text{C}_6\text{H}_{13}$   
 ClHgO $_2 \cdot \text{S} \cdot \text{C}_7\text{H}_7$   
 ClHgO $_2 \cdot \text{S} \cdot \text{C}_{12}\text{H}_{13}$   
 ClHgO $_3 \cdot \text{C}_6\text{H}_{13}$   
 ClHgO $_3 \cdot \text{Re} \cdot \text{C}_8\text{H}_4$   
 ClHgO $_3 \cdot \text{C}_3\text{H}_7$   
 ClHgPb $\cdot \text{C}_{18}\text{H}_{15}$   
 ClHgS $\cdot \text{C}_4\text{H}_3$   
 ClHgSi $\cdot \text{C}_4\text{H}_{11}$   
 ClHgSi $\cdot \text{C}_8\text{H}_{17}$   
 ClHgSn $\cdot \text{C}_{18}\text{H}_{15}$   
**ClK**

KCl

Electrolyte: 5.5.7.1.3

**CLi**

LiCl

Formation: 5.5.7.4

CLi $\cdot \text{CHBr}$   
 CLi $\cdot \text{CH}_2$   
 CLi $\cdot \text{C}_2\text{H}_2$   
 CLi $\cdot \text{C}_3\text{H}_4$   
 CLi $\cdot \text{C}_4\text{H}_6$   
 CLi $\cdot \text{C}_6\text{H}_4$   
 CLi $\cdot \text{C}_7\text{H}_8$   
 CLi $\cdot \text{C}_8\text{H}_6$   
 CLi $\cdot \text{C}_{11}\text{H}_{10}$   
 CLiN $\cdot \text{C}_7\text{H}_3$   
 CLiN $\cdot \text{C}_9\text{H}_{11}$   
 CLiN $_2\text{OP} \cdot \text{C}_5\text{H}_{13}$   
 CLiO $\cdot \text{C}_4\text{H}_4$   
 CLiO $\cdot \text{C}_4\text{H}_6$   
 CLiO $\cdot \text{C}_{12}\text{H}_8$   
 CLiOS $\cdot \text{C}_7\text{H}_6$   
 CLiO $_2 \cdot \text{C}_6\text{H}_8$   
 CLiO $_2\text{PS} \cdot \text{C}_7\text{H}_{11}$   
 CLiO $_2\text{Si} \cdot \text{C}_9\text{H}_{18}$   
 CLiO $_3\text{P} \cdot \text{C}_5\text{H}_{11}$   
 CLiO $_6\text{P}_2 \cdot \text{C}_9\text{H}_{20}$   
 CLiS $\cdot \text{C}_4\text{H}_2$   
 CLiSi $\cdot \text{C}_4\text{H}_{10}$   
 CLiSi $\cdot \text{C}_6\text{H}_{12}$   
 CLiSi $\cdot \text{C}_8\text{H}_{18}$   
 CLiSn $\cdot \text{C}_4\text{H}_9\text{Br}$   
 CLi $_2\text{NO} \cdot \text{C}_{10}\text{H}_{12}$   
 ClMg $\cdot \text{C}_3\text{H}_7$   
 ClMg $\cdot \text{C}_4\text{H}_7$   
 ClMg $\cdot \text{C}_4\text{H}_9$   
 ClMg $\cdot \text{C}_5\text{H}_{12}\text{As}$   
 ClMg $\cdot \text{C}_6\text{H}_4\text{Br}$   
 ClMg $\cdot \text{C}_7\text{H}_7$   
 ClMg $\cdot \text{C}_7\text{H}_{13}$   
 ClMgO $\cdot \text{C}_5\text{H}_{11}$   
 ClMgS $\cdot \text{C}_5\text{H}_{11}$   
 ClMgSi $\cdot \text{C}_4\text{H}_{11}$

**CLNa**

NaCl

Electrolyte: 5.5.7.1.3

CLNaO $_2 \cdot \text{C}_2\text{H}_8$   
 ClOZn $\cdot \text{CH}_3$   
 ClP $\cdot \text{C}_{18}\text{H}_{15}\text{Au}$   
 ClP $_2\text{Si}_2 \cdot \text{C}_{17}\text{H}_{38}\text{Ag}$   
 ClP $_3 \cdot \text{C}_{54}\text{H}_{45}\text{Ag}$   
 ClP $_3 \cdot \text{C}_{54}\text{H}_{45}\text{Au}$   
 ClPb $\cdot \text{C}_3\text{H}_9$   
 ClPb $\cdot \text{C}_{18}\text{H}_{15}$   
 ClPb $\cdot \text{C}_{21}\text{H}_{19}$



$\text{ClPb}^*\text{C}_{21}\text{H}_{21}$   
 $\text{ClPb}^*\text{C}_{22}\text{H}_{21}$   
 $\text{ClPbSi}^*\text{C}_{24}\text{H}_{27}$   
 $\text{ClSi}^*\text{C}_4\text{H}_3$   
 $\text{ClSi}^*\text{C}_5\text{H}_7$   
 $\text{ClSi}^*\text{C}_3\text{H}_9$   
 $\text{ClSi}^*\text{C}_4\text{H}_{11}$   
 $\text{ClSi}^*\text{C}_6\text{H}_{11}$   
 $\text{ClSi}^*\text{C}_{12}\text{H}_{11}$   
 $\text{ClSi}^*\text{C}_{12}\text{H}_{19}$   
 $\text{ClSi}^*\text{C}_{13}\text{H}_{13}$   
 $\text{ClSi}^*\text{C}_{16}\text{H}_{19}$   
 $\text{ClSi}^*\text{C}_{18}\text{H}_{15}$   
 $\text{ClSi}^*\text{C}_{20}\text{H}_{19}$   
 $\text{ClSi}^*\text{C}_{21}\text{H}_{21}$   
 $\text{ClSn}^*\text{C}_3\text{H}_9$   
 $\text{ClSn}^*\text{C}_5\text{H}_{11}$   
 $\text{ClSn}^*\text{C}_6\text{H}_{15}$   
 $\text{ClSn}^*\text{C}_{18}\text{H}_{15}$   
 $\text{ClSn}^*\text{C}_{18}\text{H}_{15}\text{Cd}$   
 $\text{ClSn}^*\text{C}_{21}\text{H}_{21}$   
 $\text{ClSnZn}^*\text{C}_{13}\text{H}_{13}$   
 $\text{ClSnZn}^*\text{C}_{18}\text{H}_{15}$   
 $\text{ClSn}_2^*\text{C}_7\text{H}_{18}\text{Br}$   
 $\text{ClZn}^*\text{C}_2\text{H}_5$   
 $\text{ClZn}^*\text{C}_4\text{H}_7$   
 $\text{ClZn}^*\text{C}_7\text{H}_7$   
 $\text{ClZn}^*\text{C}_8\text{H}_5$   
 $\text{ClZn}^*\text{C}_{10}\text{H}_7$   
 $\text{ClZn}^*\text{C}_{12}\text{H}_{10}\text{Au}$   
 $\text{Cl}_2^*\text{C}_{12}\text{H}_8\text{Cd}$   
 $\text{Cl}_2^*\text{Ca}$   
 $\text{Cl}_2^*\text{Cd}$   
 $\text{Cl}_2\text{FHg}_2\text{O}^*\text{C}_{15}\text{H}_{11}$   
 $\text{Cl}_2\text{FLi}^*\text{C}$   
 $\text{Cl}_2\text{F}_3\text{Hg}_2^*\text{C}_7\text{H}_3$   
 $\text{Cl}_2\text{F}_3\text{NZn}^*\text{C}_{13}\text{H}_{28}$   
 $\text{Cl}_2\text{F}_4\text{Hg}_2^*\text{C}_6$   
 $\text{Cl}_2\text{F}_5^*\text{C}_{24}\text{H}_{15}\text{Au}$   
 $\text{Cl}_2\text{F}_6\text{Hg}^*\text{C}_4\text{H}_2$   
 $\text{Cl}_2\text{FeHg}^*\text{C}_{10}\text{H}_8$   
 $\text{Cl}_2\text{FeHg}_2^*\text{C}_{10}\text{H}_8$   
 $\text{Cl}_2\text{Ge}^*\text{C}_8\text{H}_{18}$   
 $\text{Cl}_2\text{GePb}^*\text{C}_{37}\text{H}_{30}$   
 $\text{Cl}_2\text{Hg}$

$\text{HgCl}_2$

Reaction with  $\text{ArNH}_2$ : 5.7.2.3.6  
 Reaction with  $(\text{C}_6\text{H}_5)_5\text{PbX}$ : 5.7.6.2  
 Reaction with  $(\text{C}_6\text{H}_5)_6\text{Pb}_2$ : 5.7.6.2  
 Reaction with  $\text{RAg}$ : 5.7.2.3.1  
 Reaction with  $\text{RAu}$ : 5.7.2.3.1  
 Reaction with  $\text{RCu}$ : 5.7.2.3.1

Reaction with  $\text{RSO}_2\text{M}$ : 5.7.2.3.7  
 Reaction with  $\text{R}_2\text{CN}_2$ : 5.7.2.3.5  
 Reaction with  $\text{RB(OR')}_2$ : 5.7.2.3.7  
 Reaction with  $(\text{R}_3\text{Ge})_2\text{Hg}$ : 5.7.4.6  
 Reaction with  $\text{R}_3\text{GeGeR}_3$ : 5.7.4.5  
 Reaction with  $(\text{R}_3\text{Si})_2\text{Cd}$ : 5.7.3.5  
 Reaction with  $(\text{C}_6\text{H}_5)_3\text{PbLi}$ : 5.7.6.2  
 Reaction with  $\text{RLi}$ : 5.7.2.3.1  
 Reaction with  $\text{R}_6\text{Sn}_2$ : 5.7.5.4  
 Reaction with aliphatics: 5.7.2.3.4  
 Reaction with alkenes: 5.7.2.3.3  
 Reaction with alkynes: 5.7.2.3.3  
 Reaction with arenes: 5.7.2.3.4  
 Reaction with carboxylates: 5.7.2.3.7  
 Reaction with ketenes: 5.7.2.3.3

$\text{Cl}_2\text{Hg}^*\text{C}_2\text{H}_2$   
 $\text{Cl}_2\text{Hg}^*\text{C}_2\text{H}_4$   
 $\text{Cl}_2\text{Hg}^*\text{C}_3\text{H}_4$   
 $\text{Cl}_2\text{Hg}^*\text{C}_4\text{H}_4$   
 $\text{Cl}_2\text{Hg}^*\text{C}_4\text{H}_8$   
 $\text{Cl}_2\text{Hg}^*\text{C}_6\text{H}_3\text{Br}$   
 $\text{Cl}_2\text{Hg}^*\text{C}_6\text{H}_4$   
 $\text{Cl}_2\text{Hg}^*\text{C}_{12}\text{Br}_8$   
 $\text{Cl}_2\text{Hg}^*\text{C}_{12}\text{H}_8$   
 $\text{Cl}_2\text{Hg}^*\text{C}_{13}\text{H}_{10}$   
 $\text{Cl}_2\text{Hg}^*\text{C}_{14}\text{H}_{12}$   
 $\text{Cl}_2\text{Hg}^*\text{C}_{26}\text{H}_{20}$   
 $\text{Cl}_2\text{HgO}^*\text{C}_2\text{H}_2$   
 $\text{Cl}_2\text{HgO}_2^*\text{C}_6\text{H}_6$   
 $\text{Cl}_2\text{HgO}_2\text{S}^*\text{C}_6\text{H}_4$   
 $\text{Cl}_2\text{HgO}_2\text{S}^*\text{C}_{12}\text{H}_8$   
 $\text{Cl}_2\text{HgO}_4^*\text{C}_{14}\text{Br}_8$   
 $\text{Cl}_2\text{HgPb}^*\text{C}_{25}\text{H}_{20}$   
 $\text{Cl}_2\text{HgSi}_2^*\text{C}_4\text{H}_{12}$   
 $\text{Cl}_2\text{HgSn}^*\text{C}_6\text{H}_{14}$   
 $\text{Cl}_2\text{Hg}_2$

$\text{Hg}_2\text{Cl}_2$

Reaction with  $\text{RLi}$ : 5.7.2.3.1

$\text{Cl}_2\text{Hg}_2^*\text{CH}_2$   
 $\text{Cl}_2\text{Hg}_2^*\text{C}_{16}\text{H}_{14}$   
 $\text{Cl}_2\text{Hg}_2\text{N}_2^*\text{C}_3$   
 $\text{Cl}_2\text{Hg}_2\text{O}^*\text{C}_4\text{H}_2$   
 $\text{Cl}_2\text{Hg}_2\text{O}^*\text{C}_4\text{H}_8$   
 $\text{Cl}_2\text{Hg}_2\text{O}^*\text{C}_{12}\text{H}_{11}$   
 $\text{Cl}_2\text{Hg}_2\text{O}_2^*\text{C}_4\text{H}_8$   
 $\text{Cl}_2\text{Hg}_2\text{O}_2^*\text{C}_6\text{H}_{12}$   
 $\text{Cl}_2\text{Hg}_2\text{O}_2^*\text{C}_{11}\text{H}_{18}$   
 $\text{Cl}_2\text{Hg}_2\text{O}_2^*\text{C}_{16}\text{H}_{16}$   
 $\text{Cl}_2\text{Hg}_2\text{S}^*\text{C}_4\text{H}_2$   
 $\text{Cl}_2\text{Li}^*\text{CBr}$   
 $\text{Cl}_2\text{Li}^*\text{CH}$   
 $\text{Cl}_2\text{Li}^*\text{C}_2\text{H}$

- $\text{Cl}_2\text{Li}^*\text{C}_2\text{H}_3$   
 $\text{Cl}_2\text{Li}^*\text{C}_3\text{H}_3$   
 $\text{Cl}_2\text{Li}^*\text{C}_7\text{H}_5$   
 $\text{Cl}_2\text{LiO}_2^*\text{C}_4\text{H}_5$   
 $\text{Cl}_2\text{LiO}_3\text{P}^*\text{C}_5\text{H}_{10}$   
 $\text{Cl}_2\text{LiPb}^*\text{C}_{19}\text{H}_{15}$   
 $\text{Cl}_2\text{LiSi}^*\text{C}_4\text{H}_9$   
 $\text{Cl}_2\text{LiSi}^*\text{C}_6\text{H}_{11}$   
 $\text{Cl}_2\text{LiSn}^*\text{C}_4\text{H}_9$   
 $\text{Cl}_2\text{Li}_2\text{O}_2^*\text{C}_2$   
 $\text{Cl}_2\text{Mg}^*\text{C}_6\text{H}_3\text{Br}$   
 $\text{Cl}_2\text{Mg}^*\text{C}_7\text{H}_6$   
 $\text{Cl}_2\text{NZn}^*\text{C}_{13}\text{H}_{31}$   
 $\text{Cl}_2\text{NZn}^*\text{C}_{14}\text{H}_{33}$   
 $\text{Cl}_2\text{NZn}^*\text{C}_{18}\text{H}_{33}$   
 **$\text{Cl}_2\text{Pb}$**   
 $\text{PbCl}_2$   
 Electrolyte: 5.7.6.1.3  
 Reaction with  $\text{PhLi}$ : 5.5.7.2.2, 5.5.7.5  
 Reaction with  $\text{Zn}$  metal: 5.7.6.1.2  
 $\text{Cl}_2\text{Pb}^*\text{C}_2\text{H}_6$   
 $\text{Cl}_2\text{Pb}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Cl}_2\text{Pb}^*\text{C}_{21}\text{H}_{18}$   
 $\text{Cl}_2\text{PbSi}^*\text{C}_{37}\text{H}_{30}$   
 $\text{Cl}_2\text{PbSn}^*\text{C}_{37}\text{H}_{30}$   
 $\text{Cl}_2\text{Pb}_2^*\text{C}_{37}\text{H}_{30}$   
 $\text{Cl}_2\text{S}^*\text{C}_{12}\text{H}_{19}\text{Au}$   
 $\text{Cl}_2\text{Si}^*\text{CH}_4$   
 $\text{Cl}_2\text{Si}_2^*\text{C}_4\text{H}_{12}$   
 $\text{Cl}_2\text{Si}_2^*\text{C}_5\text{H}_{14}$   
 **$\text{Cl}_2\text{Sn}$**   
 $\text{SnCl}_2$   
 Reaction with  $\text{RLi}$ : 5.5.6.2.1, 5.5.6.6  
 Reaction with  $\text{R}_3\text{SnLi}$ : 5.5.6.6  
 $\text{Cl}_2\text{Sn}^*\text{C}_4\text{H}_{10}$   
 $\text{Cl}_2\text{Sn}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Cl}_2\text{Sn}_2^*\text{C}_7\text{H}_{18}$   
 **$\text{Cl}_2\text{Zn}$**   
 $\text{ZnCl}_2$   
 Formation: 5.7.6.1.2  
 Reaction with  $\text{Ar}_3\text{SiK}$ : 5.7.3.1  
 Reaction with  $\text{RLi}$ : 5.7.2.3.1  
 Reaction with  $\text{RMgX}$ : 5.7.2.3.1  
 Reaction with  $\text{RNa}$ : 5.7.2.3.1  
 Reaction with  $\text{RK}$ : 5.7.2.3.1  
 Reaction with  $\text{R}_2\text{Zn}$ : 5.7.2.3.2  
 Reaction with  $\text{R}_3\text{GeNa}$ : 5.7.4.1  
 Reaction with  $\text{R}_3\text{SnK}$ : 5.7.5  
 $\text{Cl}_2\text{Zn}^*\text{C}_2\text{H}_4$   
 $\text{Cl}_2\text{Zn}^*\text{C}_{12}\text{H}_8$   
 $\text{Cl}_3^*\text{C}_{18}\text{H}_{12}\text{Bi}$   
 $\text{Cl}_3\text{CuP}_3\text{Sn}^*\text{C}_{54}\text{H}_{45}$
- $\text{Cl}_3\text{F}_3\text{Zn}^*\text{C}_2$   
 **$\text{Cl}_3\text{GeH}$**   
 $\text{Cl}_3\text{GeH}$   
 Reaction with  $\text{R}_2\text{Hg}$ : 5.7.4.2  
 $\text{Cl}_3\text{GeHgSi}^*\text{C}_3\text{H}_9$   
 $\text{Cl}_3\text{GeHgSi}^*\text{C}_4\text{H}_{11}$   
 **$\text{Cl}_3\text{HSi}$**   
 $\text{Cl}_3\text{SiH}$   
 Reaction with  $\text{R}_2\text{Hg}$ : 5.7.3.3  
 $\text{Cl}_3\text{Hg}^*\text{CBr}$   
 $\text{Cl}_3\text{Hg}^*\text{C}_2\text{H}_2\text{Br}$   
 $\text{Cl}_3\text{Hg}^*\text{C}_3\text{H}_3$   
 $\text{Cl}_3\text{Hg}^*\text{C}_6\text{H}_3$   
 $\text{Cl}_3\text{Hg}^*\text{C}_7\text{H}_5$   
 **$\text{Cl}_3\text{HgISI}$**   
 $\text{Cl}_3\text{SiHgI}$   
 Formation: 5.7.3.3  
 $\text{Cl}_3\text{HgO}_2^*\text{C}_4\text{H}_5$   
 $\text{Cl}_3\text{HgSi}^*\text{Br}$   
 $\text{Cl}_3\text{HgSi}^*\text{C}_2\text{H}_5$   
 $\text{Cl}_3\text{HgSi}_2^*\text{C}_3\text{H}_9$   
 $\text{Cl}_3\text{Hg}_3^*\text{CH}$   
 $\text{Cl}_3\text{Li}^*\text{C}$   
 $\text{Cl}_3\text{Li}^*\text{C}_2$   
 $\text{Cl}_3\text{Li}^*\text{C}_6\text{H}_2$   
 $\text{Cl}_3\text{LiS}^*\text{C}_4$   
 $\text{Cl}_3\text{PSn}^*\text{C}_{18}\text{H}_{15}\text{Au}$   
 $\text{Cl}_3\text{P}_2\text{Sn}^*\text{C}_{36}\text{H}_{30}\text{Au}$   
 $\text{Cl}_3\text{P}_3\text{Sn}^*\text{C}_{54}\text{H}_{45}\text{Ag}$   
 $\text{Cl}_3\text{P}_3\text{Sn}^*\text{C}_{54}\text{H}_{45}\text{Au}$   
 $\text{Cl}_3\text{P}_4\text{Sn}^*\text{C}_{72}\text{H}_{60}\text{Au}_4$   
 $\text{Cl}_3\text{Sb}^*\text{C}_6\text{H}_4$   
 $\text{Cl}_3\text{Sb}^*\text{C}_{18}\text{H}_{12}$   
 $\text{Cl}_3\text{Si}_2^*\text{C}_3\text{H}_9$   
 $\text{Cl}_4^*\text{C}$   
 $\text{Cl}_4^*\text{C}_{12}\text{H}_{10}\text{Au}_2$   
 $\text{Cl}_4\text{F}_6\text{Zn}^*\text{C}_4$   
 **$\text{Cl}_4\text{Ge}$**   
 $\text{GeCl}_4$   
 Reaction with  $(\text{R}_3\text{Si})_2\text{Hg}$ : 5.7.4.7  
 $\text{Cl}_4\text{Hg}^*\text{C}_{12}\text{H}_6$   
 $\text{Cl}_4\text{HgSi}_2^*\text{C}_2\text{H}_6$   
 $\text{Cl}_4\text{Hg}_3\text{O}_4^*\text{C}_8\text{H}_{10}$   
 $\text{Cl}_4\text{Hg}_4^*\text{C}$   
 $\text{Cl}_4\text{Li}^*\text{C}_6\text{H}$   
 $\text{Cl}_4\text{Li}^*\text{C}_5$   
 $\text{Cl}_4\text{Li}_2^*\text{C}_6$   
 $\text{Cl}_4\text{NSi}^*\text{C}_7\text{H}_7$   
 **$\text{Cl}_4\text{Si}$**   
 $\text{SiCl}_4$   
 Reaction with  $\text{Li}$  metal: 5.5.4.3  
 **$\text{Cl}_4\text{Sn}$**   
 $\text{SnCl}_4$   
 Reaction with  $\text{Au-Ge}$  bonds: 5.6.5.4

- $\text{Cl}_5\text{Hg}^*\text{C}_{11}\text{H}_5$   
 $\text{Cl}_5\text{Hg}^*\text{C}_{12}\text{H}_5$   
 $\text{Cl}_5\text{Hg}^*\text{C}_{13}\text{H}_7$   
 $\text{Cl}_5\text{HgO}_2^*\text{C}_{13}\text{H}_5$   
 $\text{Cl}_5\text{HgO}_2^*\text{C}_{14}\text{H}_7$   
 $\text{Cl}_5\text{Li}^*\text{C}_6$   
 $\text{Cl}_5\text{Mg}^*\text{C}_6\text{Br}$   
 $\text{Cl}_5\text{Si}^*\text{C}_8\text{H}_7$   
 $\text{Cl}_6^*\text{Au}_2$   
 $\text{Cl}_6\text{Ge}_2$   
 $\text{Cl}_3\text{GeGeCl}_3$   
 Formation: 5.7.4.7  
 $\text{Cl}_6\text{Ge}_2\text{Hg}$   
 $(\text{Cl}_3\text{Ge})_2\text{Hg}$   
 Formation: 5.7.4, 5.7.4.2  
 $\text{Cl}_6\text{H}_8\text{N}_2\text{Pb}$   
 $[(\text{NH}_4)]_2[\text{PbCl}_6]$   
 Starting material for  $\text{Ph}_3\text{PbX}$ : 5.5.7.4  
 $\text{Cl}_6\text{Hg}^*\text{C}_2$   
 $\text{Cl}_6\text{Hg}^*\text{C}_4$   
 $\text{Cl}_6\text{Hg}^*\text{C}_6$   
 $\text{Cl}_6\text{Hg}^*\text{C}_{12}\text{H}_4$   
 $\text{Cl}_6\text{HgSi}_2$   
 $(\text{Cl}_3\text{Si})_2\text{Hg}$   
 Formation: 5.7.3.3  
 Thermal decomposition: 5.7.3.3  
 $\text{Cl}_6\text{Li}^*\text{C}_7\text{Br}$   
 $\text{Cl}_6\text{Si}_2$   
 $\text{Si}_2\text{Cl}_6$   
 Formation: 5.7.3.3  
 $\text{Cl}_7\text{LiSi}_2^*\text{C}$   
 $\text{Cl}_8\text{Hg}^*\text{C}_{12}\text{H}_2$   
 $\text{Cl}_8\text{HgN}_2\text{O}_4^*\text{C}_{12}$   
 $\text{Cl}_8\text{HgN}_2\text{O}_6\text{S}_2^*\text{C}_{22}\text{H}_{12}$   
 $\text{Cl}_8\text{HgO}_8\text{S}_2^*\text{C}_{12}\text{H}_6$   
 $\text{Cl}_{10}\text{Hg}^*\text{C}_{10}$   
 $\text{Cl}_{10}\text{Hg}^*\text{C}_{12}$   
 $\text{Cl}_{10}\text{HgO}_4^*\text{C}_{14}$   
 $\text{Cl}_{10}\text{HgO}_8\text{S}_2^*\text{C}_{12}\text{H}_4$   
 $\text{Cl}_{12}\text{Hg}_2\text{O}_6\text{S}_2^*\text{C}_{18}\text{H}_2$   
 $\text{CoLiSn}^*\text{C}_{39}\text{H}_{30}$   
 $\text{CoSn}_2^*\text{C}_{57}\text{H}_{45}$   
 $\text{CrHgO}_3^*\text{C}_9\text{H}_5\text{Cl}$   
 $\text{CrLiO}_3^*\text{C}_9\text{H}_5$   
 $\text{CrLiO}_4\text{S}^*\text{C}_{21}\text{H}_{15}$   
 $\text{CrLiO}_4\text{Si}^*\text{C}_{18}\text{H}_{25}$   
 $\text{CrN}_3\text{O}_3^*\text{C}_3\text{H}_9$   
 $\text{CrO}_3^*\text{C}_9\text{H}_6$   
 $\text{CrO}_4^*\text{C}_9\text{H}_7\text{B}$   
 $\text{Cr}_2\text{HgO}_6^*\text{C}_{18}\text{H}_{10}$   
**Cs**  
**Cs**  
 Reaction with  $\text{R}_3\text{GeLi}$ : 5.5.5.7  
 $\text{Cs}^*\text{C}_3\text{H}_5$   
 $\text{Cs}^*\text{C}_4\text{H}_9$   
 $\text{Cs}^*\text{C}_6\text{H}_6$   
 $\text{Cs}^*\text{C}_7\text{H}_7$   
 $\text{Cs}^*\text{C}_8$   
 $\text{Cs}^*\text{C}_8\text{H}_9$   
 $\text{Cs}^*\text{C}_{13}\text{H}_{11}$   
 $\text{Cs}^*\text{C}_{13}\text{H}_{15}$   
 $\text{Cs}^*\text{C}_{18}\text{H}_{21}$   
 $\text{Cs}^*\text{C}_{19}\text{H}_{15}$   
 $\text{Cs}^*\text{C}_{21}\text{H}_{19}$   
 $\text{Cs}^*\text{C}_{24}$   
 $\text{Cs}^*\text{C}_{36}$   
 $\text{Cs}^*\text{C}_{48}$   
 $\text{Cs}^*\text{C}_{60}$   
**CsF**  
**CsF**  
 Reaction with  $\text{GeI}_2$ : 5.5.5.7  
**CsGe**  
**CsGe**  
 Formation: 5.5.5.1  
 $\text{CsGe}^*\text{C}_6\text{H}_{15}$   
**CsGeH<sub>3</sub>**  
 $\text{Cs}[\text{H}_3\text{Ge}]$   
 Formation: 5.5.5.4  
 $\text{CsN}^*\text{C}_6\text{H}_{12}$   
 $\text{CsN}^*\text{C}_6\text{H}_{14}$   
 $\text{CsO}^*\text{C}_4\text{H}_9$   
**CsPb**  
**CsPb**  
 Formation: 5.5.7.1.1  
**CsSi**  
**CsSi**  
 Formation: 5.5.4.1  
 $\text{CsSi}^*\text{C}_4\text{H}_{11}$   
 $\text{CsSi}^*\text{C}_6\text{H}_{15}$   
 $\text{CsSi}^*\text{C}_{18}\text{H}_{15}$   
**CsSn**  
**CsSn**  
 Formation: 5.5.6.1.5  
 $\text{Cs}_2^*\text{C}_{12}\text{H}_{10}$   
 $\text{Cs}_2^*\text{C}_{12}\text{H}_{12}$   
**Cu**  
**Cu**  
 Reaction with  $\text{HC}\equiv\text{CPh}$ : 5.6.4.3  
 $\text{Cu}^*\text{Br}$   
 $\text{Cu}^*\text{C}_6\text{H}_4\text{Cl}$   
 $\text{Cu}^*\text{C}_6\text{H}_5$   
 $\text{Cu}^*\text{C}_7\text{H}_7$   
 $\text{Cu}^*\text{C}_8\text{H}_9$   
 $\text{Cu}^*\text{C}_{36}\text{H}_{34}\text{B}$   
 $\text{Cu}^*\text{C}_{37}\text{H}_{33}$

$\text{Cu}^*\text{C}_{104}\text{H}_{80}$   
 $\text{CuF}_3^*\text{C}_7\text{H}_4$   
 $\text{CuF}_3\text{O}_3\text{S}^*\text{C}$   
 $\text{CuF}_3^*\text{C}_6$   
 $\text{CuF}_9^*\text{C}_4$   
 $\text{CuF}_{10}\text{Li}^*\text{C}_{12}$   
 $\text{CuF}_{15}^*\text{C}_7$   
 $\text{CuGeP}_3^*\text{C}_{72}\text{H}_{60}$   
 $\text{CuHgP}^*\text{C}_{19}\text{H}_{16}\text{Br}_2$   
 $\text{CuLi}^*\text{C}_2\text{H}_6$   
 $\text{CuLiN}_2^*\text{C}_{18}\text{H}_{24}$   
 $\text{CuMnO}_3^*\text{C}_8\text{H}_4$   
 $\text{CuMnO}_6^*\text{C}_{16}\text{H}_8\text{Ag}$   
 $\text{CuN}^*\text{C}$   
 $\text{CuN}^*\text{C}_8\text{H}_{10}$   
 $\text{CuN}^*\text{C}_{39}\text{H}_{34}$   
 $\text{CuNO}_2^*\text{C}_3\text{H}_2$   
 $\text{CuNP}^*\text{C}_{20}\text{H}_{32}$   
 $\text{CuNP}_2^*\text{C}_{38}\text{H}_{32}$   
 $\text{CuNS}^*\text{C}$   
 $\text{CuN}_2^*\text{C}_{18}\text{H}_{13}$   
 $\text{CuN}_2^*\text{C}_{39}\text{H}_{31}$   
 $\text{CuN}_2\text{O}_4\text{P}_2^*\text{C}_{42}\text{H}_{35}$   
 $\text{CuO}^*\text{C}_7\text{H}_7$   
 $\text{CuOP}^*\text{C}_{10}\text{H}_{24}$   
 $\text{CuO}_2^*\text{C}_{10}\text{H}_{14}$   
 $\text{CuO}_2\text{P}_2^*\text{C}_{40}\text{H}_{35}$   
 $\text{CuP}^*\text{C}_{11}\text{H}_{20}$   
 $\text{CuP}^*\text{C}_{18}\text{H}_{15}\text{Br}$   
 $\text{CuP}^*\text{C}_{23}\text{H}_{20}$   
 $\text{CuP}_2^*\text{C}_{37}\text{H}_{33}$   
 $\text{CuP}_2^*\text{C}_{38}\text{H}_{35}$   
 $\text{CuP}_2^*\text{C}_{39}\text{H}_{37}$   
 $\text{CuP}_2^*\text{C}_{40}\text{H}_{39}$   
 $\text{CuP}_3^*\text{C}_{54}\text{H}_{45}\text{Cl}$   
 $\text{CuP}_3\text{Sn}^*\text{C}_{54}\text{H}_{45}\text{Cl}_3$

**CuZn**

Zn-Cu

Reaction with RX: 5.7.2.2.1

 $\text{Cu}_2\text{Li}_2\text{N}_4^*\text{C}_{36}\text{H}_{48}$  $\text{Cu}_2\text{N}_2^*\text{C}_{18}\text{H}_{20}$  $\text{Cu}_2\text{N}_4^*\text{C}_{22}\text{H}_{30}$ **Cu<sub>2</sub>O** $\text{Cu}_2\text{O}$ 

Reaction with RH: 5.6.4.3

Reaction with  $\text{C}_5\text{H}_6$ : 5.6.4 $\text{Cu}_2\text{P}_2^*\text{C}_8\text{H}_{20}$  $\text{Cu}_2\text{P}_6^*\text{C}_{50}\text{H}_{72}$  $\text{Cu}_2\text{P}_6^*\text{C}_{52}\text{H}_{76}$  $\text{Cu}_2\text{P}_6^*\text{C}_{54}\text{H}_{80}$  $\text{Cu}_2\text{P}_6^*\text{C}_{54}\text{H}_{84}$ **Cu<sub>3</sub>Ge** $\text{Cu}_3\text{Ge}$ 

Formation: 5.6.2

 $\text{Cu}_3\text{P}_6^*\text{C}_{75}\text{H}_{63}$ **Cu<sub>3</sub>Sn** $\text{SnCu}_3$ 

Formation: 5.6.2

 $\text{Cu}_4^*\text{C}_{28}\text{H}_{28}$  $\text{Cu}_4\text{F}_{12}^*\text{C}_{28}\text{H}_{16}$  $\text{Cu}_4\text{F}_{20}^*\text{C}_{24}$  $\text{Cu}_4\text{I}_4\text{P}_4^*\text{C}_{48}\text{H}_{108}$  $\text{Cu}_4\text{I}_4\text{P}_4^*\text{C}_{72}\text{H}_{60}$  $\text{Cu}_4\text{Mg}^*\text{C}_{36}\text{H}_{30}$  $\text{Cu}_4\text{N}_2^*\text{C}_{36}\text{H}_{40}\text{Br}_2$  $\text{Cu}_4\text{N}_4^*\text{C}_{36}\text{H}_{48}$  $\text{Cu}_4\text{N}_4^*\text{C}_{40}\text{H}_{56}$  $\text{Cu}_4\text{Si}_4^*\text{C}_{16}\text{H}_{44}$ **Cu<sub>5</sub>Si** $\text{Cu}_5\text{Si}$ 

Formation: 5.6.2

 $\text{Cu}_6\text{N}_4^*\text{C}_{32}\text{H}_{40}\text{Br}_2$  $\text{Cu}_6\text{N}_4^*\text{C}_{50}\text{H}_{54}$ **Cu<sub>6</sub>Si** $\text{Cu}_6\text{Si}$ 

Formation: 5.6.2

**Cu<sub>18</sub>Si<sub>4</sub>** $\text{Cu}_{15}\text{Si}_4$ 

Formation: 5.6.2

 $\text{DBrMg}^*\text{CH}_2$  $\text{D}_2\text{ClHg}^*\text{C}_6\text{H}_{11}$  $\text{D}_2\text{HgN}^*\text{C}_5\text{H}_3$  $\text{D}_2\text{HgO}_3^*\text{C}_5\text{H}_8$  $\text{D}_2\text{Li}^*\text{C}_5\text{H}_7$  $\text{D}_2\text{Zn}^*\text{C}_2\text{H}_4$  $\text{D}_3\text{BrHg}^*\text{C}$  $\text{D}_3\text{ClHg}^*\text{C}$  $\text{D}_3\text{HgI}^*\text{C}$  $\text{D}_3\text{BrMg}^*\text{C}_6$  $\text{D}_6\text{Hg}^*\text{C}_2$  $\text{D}_{10}\text{Hg}^*\text{C}_{12}$  $\text{F}^*\text{Ag}$  $\text{F}^*\text{C}_6\text{H}_5$  $\text{F}^*\text{Cs}$  $\text{FGe}^*\text{C}_{18}\text{H}_{15}$  $\text{FHg}^*\text{CH}_3$  $\text{FHgO}^*\text{C}_{15}\text{H}_{12}\text{Cl}$  $\text{FHg}_2\text{O}^*\text{C}_{15}\text{H}_{11}\text{Cl}_2$ **FK**

KF

Electrolyte: 5.5.7.1.3

Reaction with  $\text{GeI}_2$ : 5.5.5.7 $\text{FLi}^*\text{CBr}_2$  $\text{FLi}^*\text{CCl}_2$  $\text{FLi}^*\text{C}_6\text{H}_4$  $\text{FLi}^*\text{C}_7\text{H}_6$

- $\text{FLi}^*\text{C}_9\text{H}_8$   
 $\text{FLiO}^*\text{C}_7\text{H}_6$   
 $\text{FLiS}^*\text{C}_4\text{H}_2$   
 $\text{FLiS}^*\text{C}_6\text{H}_9\text{Cl}$   
 $\text{FLiSi}^*\text{C}_9\text{H}_{11}\text{Cl}$   
**FNa**  
     NaF  
         Electrolysis: 5.5.7.1.3  
**FRb**  
     RbF  
         Reaction with  $\text{GeI}_2$ : 5.5.5.7  
 $\text{FSi}^*\text{C}_{18}\text{H}_{15}$   
**F<sub>2</sub>Ge**  
      $\text{GeF}_2$   
         Reaction with  $(\text{R}_3\text{Ge})_2\text{Hg}$ : 5.7.4.8  
         Reaction with  $\text{R}_2\text{Hg}$ : 5.7.4.8  
         Reaction with  $(\text{R}_3\text{Ge})_2\text{Hg}$ : 5.7.4.8  
 $\text{F}_2\text{Ge}_3^*\text{C}_{36}\text{H}_{30}$   
 $\text{F}_2\text{Ge}_3\text{Hg}^*\text{C}_{36}\text{H}_{30}$   
 $\text{F}_2\text{Hg}^*\text{C}_{12}\text{Br}_8$   
 $\text{F}_2\text{Hg}^*\text{C}_{12}\text{H}_8$   
 $\text{F}_2\text{HgN}_4\text{O}_8^*\text{C}_2$   
 $\text{F}_2\text{HgO}_4^*\text{C}_{14}\text{Br}_8$   
 $\text{F}_2\text{HgO}_4\text{S}_2^*\text{C}_{12}\text{H}_8$   
**F<sub>2</sub>Hg<sub>2</sub>**  
      $\text{FHgHgF}$   
         Reaction with  $\text{R}_2\text{Hg}$ : 5.7.2.3.2  
 $\text{F}_2\text{Li}^*\text{C}_2\text{H}$   
 $\text{F}_2\text{Li}^*\text{C}_3\text{H}_3$   
 $\text{F}_2\text{O}_3\text{P}^*\text{C}_5\text{H}_{10}\text{BrCd}$   
 $\text{F}_2\text{Sn}^*\text{C}_6\text{H}_{12}$   
 $\text{F}_2\text{Zn}^*\text{C}_{12}\text{H}_8$   
 $\text{F}_3^*\text{C}_7\text{H}_4\text{Cu}$   
 $\text{F}_3\text{Hg}^*\text{C}_7\text{H}_4\text{Cl}$   
 $\text{F}_3\text{HgI}^*\text{C}$   
 $\text{F}_3\text{HgO}_2^*\text{C}_8\text{H}_5$   
 $\text{F}_3\text{HgO}_3^*\text{C}_9\text{H}_{15}$   
 $\text{F}_3\text{Hg}_2^*\text{C}_7\text{H}_3\text{Cl}_2$   
 $\text{F}_3\text{Li}^*\text{C}_2$   
 $\text{F}_3\text{Li}^*\text{C}_3\text{H}_2$   
 $\text{F}_3\text{Li}^*\text{C}_7\text{H}_4$   
 $\text{F}_3\text{LiOSe}^*\text{C}_9\text{H}_8$   
 $\text{F}_3\text{LiS}^*\text{C}_9\text{H}_9$   
 $\text{F}_3\text{LiSe}^*\text{C}_8\text{H}_6$   
 $\text{F}_3\text{LiSe}^*\text{C}_9\text{H}_6$   
 $\text{F}_3\text{LiSe}^*\text{C}_{10}\text{H}_8$   
 $\text{F}_3\text{LiSeSi}^*\text{C}_{11}\text{H}_{14}$   
 $\text{F}_3\text{NZn}^*\text{C}_{13}\text{H}_{28}\text{Cl}_2$   
 $\text{F}_3\text{O}_3\text{S}^*\text{CAg}$   
 $\text{F}_3\text{O}_3\text{S}^*\text{CCu}$   
 $\text{F}_3\text{Zn}^*\text{C}_2\text{Cl}_3$   
 $\text{F}_4\text{Hg}^*\text{C}_6\text{BrCl}$   
 $\text{F}_4\text{Hg}^*\text{C}_{12}\text{H}_6$   
 $\text{F}_4\text{HgO}^*\text{C}_7\text{H}_3\text{Cl}$   
 $\text{F}_4\text{HgO}^*\text{C}_{14}\text{H}_{10}$   
 $\text{F}_4\text{HgO}_3^*\text{C}_{15}\text{H}_{10}$   
 $\text{F}_4\text{HgO}_4^*\text{C}_8$   
 $\text{F}_4\text{HgO}_4^*\text{C}_{14}\text{H}_6$   
 $\text{F}_4\text{Hg}_2^*\text{C}_6\text{Br}_2$   
 $\text{F}_4\text{Hg}_2^*\text{C}_6\text{Cl}_2$   
 $\text{F}_4\text{Hg}_2\text{O}_2^*\text{C}_{10}\text{H}_6$   
 $\text{F}_4\text{Li}^*\text{C}_6\text{Br}$   
 $\text{F}_4\text{Li}^*\text{C}_9\text{H}_5$   
 $\text{F}_4\text{OP}^*\text{C}_{54}\text{H}_{45}\text{Au}_3\text{B}$   
 $\text{F}_4\text{O}_2\text{P}_2^*\text{C}_{10}\text{H}_{20}\text{Cd}$   
 $\text{F}_4\text{P}_2^*\text{C}_{43}\text{H}_{37}\text{AuB}$   
 $\text{F}_5^*\text{C}_3\text{Ag}$   
 $\text{F}_5^*\text{C}_6\text{Ag}$   
 $\text{F}_5^*\text{C}_6\text{BrCd}$   
 $\text{F}_5^*\text{C}_6\text{Cu}$   
 $\text{F}_5^*\text{C}_{24}\text{H}_{15}\text{AuCl}_2$   
 $\text{F}_5\text{Hg}^*\text{C}_7\text{H}_3$   
 $\text{F}_5\text{Hg}^*\text{C}_{12}\text{H}_5$   
 $\text{F}_5\text{HgN}^*\text{C}_7$   
 $\text{F}_5\text{HgN}_3^*\text{C}_6$   
 $\text{F}_5\text{HgO}_2^*\text{C}_8\text{H}_3$   
 $\text{F}_5\text{HgO}_2^*\text{C}_{13}\text{H}_5$   
 $\text{F}_5\text{Li}^*\text{C}_6$   
 $\text{F}_5\text{Mg}^*\text{C}_6\text{Br}$   
 $\text{F}_5\text{O}_2\text{P}^*\text{C}_{25}\text{H}_{15}\text{Au}$   
 $\text{F}_5\text{P}^*\text{C}_{24}\text{H}_{15}\text{Au}$   
 $\text{F}_5\text{P}^*\text{C}_{42}\text{H}_{30}\text{Au}$   
 $\text{F}_5\text{Si}^*\text{C}_8\text{H}_7$   
 $\text{F}_5\text{Si}^*\text{C}_{18}\text{H}_{10}\text{Cl}$   
 $\text{F}_5\text{Zn}^*\text{C}_6\text{Br}$   
 $\text{F}_5\text{Zn}^*\text{C}_6\text{Cl}$   
 $\text{F}_6^*\text{C}_3$   
 $\text{F}_6\text{Hg}^*\text{C}_2$   
 $\text{F}_6\text{Hg}^*\text{C}_4$   
 $\text{F}_6\text{Hg}^*\text{C}_4\text{H}_2\text{Cl}_2$   
 $\text{F}_6\text{HgNO}_2^*\text{C}_5\text{H}_3$   
 $\text{F}_6\text{HgN}_4^*\text{C}_4$   
 $\text{F}_6\text{HgO}_2^*\text{C}_6\text{H}_5\text{Br}$   
 $\text{F}_6\text{HgO}_4^*\text{C}_4$   
 $\text{F}_6\text{Li}^*\text{C}_8\text{H}_3$   
 $\text{F}_6\text{Li}_2\text{O}^*\text{C}_9\text{H}_4$   
 $\text{F}_6\text{N}_4\text{O}_6\text{S}_2^*\text{C}_{34}\text{H}_{40}\text{Ag}_4\text{Au}_2$   
 $\text{F}_6\text{P}_2^*\text{C}_{40}\text{H}_{30}\text{Au}_2$   
 $\text{F}_6\text{Zn}^*\text{C}_4\text{Cl}_4$   
 $\text{F}_7^*\text{C}_3\text{Ag}$   
 $\text{F}_7\text{IZn}^*\text{C}_3$   
 $\text{F}_7\text{Li}^*\text{C}_3$   
 $\text{F}_7\text{N}^*\text{C}_5\text{H}_3\text{Ag}$   
 $\text{F}_8\text{Hg}^*\text{B}_2$

$F_8Hg^*C_{12}Br_2$	$F_{15}Si_3Sn_2^*C_{30}H_{33}$
$F_8Hg^*C_{12}H_2$	$F_{15}Sn^*C_{18}Br$
$F_8HgN_2^*C_{10}$	$F_{15}Sn^*C_{18}H$
$F_8HgN_2O_4^*C_{12}$	$F_{16}Hg^*C_8H_2$
$F_8HgN_2O_6S_2^*C_{22}H_{12}$	$F_{18}Hg^*C_8$
$F_8HgO_2^*C_8$	$F_{18}Hg^*C_{10}$
$F_8HgO_2^*C_{14}H_6$	$F_{18}HgO_4^*C_{10}$
$F_8HgO_3S^*C_{12}H_2$	$F_{18}Hg_6O_{12}^*C_{18}$
$F_8HgO_8S_2^*C_{12}H_6$	$F_{20}^*C_{24}Cu_4$
$F_9^*C_4Cu$	$F_{20}Ge^*C_{24}$
$F_9Hg^*C_4Cl$	$F_{20}Ge_2^*C_{24}Br_2$
$F_9Li^*C_6$	$F_{20}Zr^*C_{24}$
$F_9Si^*C_{12}H_5$	$F_{24}Hg_8O_{16}^*C_{26}$
$F_9Sn^*C_{10}H_9$	$F_{30}GeHgSn^*C_{36}$
$F_{10}^*C_5Ag$	$F_{30}Ge_2^*C_{36}$
$F_{10}^*C_{12}Cd$	$F_{30}Ge_2^*C_{36}Cd$
$F_{10}Ge^*C_{12}HBr$	$F_{30}Ge_2^*C_{38}H_5Bi$
$F_{10}Hg^*C_4$	$F_{30}Ge_2Hg^*C_{36}$
$F_{10}Hg^*C_{12}$	$F_{30}Ge_2O_2Zn^*C_{44}H_{20}$
$F_{10}HgN_2O_6S_2^*C_{22}H_{10}$	$F_{30}Ge_2P_2^*C_{72}H_{30}Cd$
$F_{10}HgO_4^*C_{14}$	$F_{30}Ge_2Zn^*C_{36}$
$F_{10}HgO_9S_2^*C_{12}H_4$	$F_{30}HgP_2PtSn_2^*C_{78}H_{36}$
$F_{10}HgSi_2^*C_{16}H_{12}$	$F_{30}HgSn_2^*C_{36}$
$F_{10}Li^*C_{12}Cu$	$F_{30}Sn_2^*C_{36}Cd$
$F_{10}P^*C_{30}H_{15}AuCl$	$F_{75}Ge_2HgPr^*C_{90}$
$F_{10}Tl^*C_{12}Br$	$Fe^*C_{10}H_8AgCl$
$F_{10}Zn^*C_{12}$	$Fe^*C_{10}H_{10}$
$F_{11}Li^*C_5$	$FeHg^*C_{10}H_8Cl_2$
$F_{12}^*C_{28}H_{16}Cu_4$	$FeHg^*C_{10}H_9Cl$
$F_{12}Hg^*C_5$	$FeHg^*C_{12}H_{11}Cl$
$F_{12}Hg^*C_6H_2$	$FeHgMnO_5^*C_{15}H_9Cl$
$F_{12}HgN_2^*C_8$	$FeHgN^*C_{13}H_{16}Cl$
$F_{12}Hg_2O_6S_2^*C_{18}H_2$	$FeHgO^*C_{12}H_{11}Br$
$F_{12}Sn^*C_8$	$FeHg_2^*C_{10}H_8Cl_2$
$F_{13}^*C_6Ag$	$FeK_2^*C_{10}H_8$
$F_{14}Hg^*C_6$	$FeLi^*C_{10}H_9$
$F_{14}Hg^*C_8$	$FeLi^*C_{11}H_{11}$
$F_{14}HgO_4^*C_{20}H_{20}$	$FeLiN^*C_{12}H_{10}$
$F_{15}^*C_7Cu$	$FeLiN^*C_{12}H_{14}$
$F_{15}Ge^*C_{18}Br$	$FeLiN^*C_{13}H_{16}$
$F_{15}Ge^*C_{18}Cl$	$FeLiN^*C_{14}H_{18}$
$F_{15}Ge^*C_{18}H$	$FeLiOP^*C_{23}H_{20}$
$F_{15}GeHg^*C_{20}H_5$	$FeLiPS^*C_{23}H_{20}$
$F_{15}GeLi^*C_{18}$	$FeLi_2N^*C_{12}H_{13}$
$F_{15}Ge_2^*C_{24}H_{15}$	$FeMnO_5^*C_{15}H_{10}$
$F_{15}Ge_2Hg^*C_{24}H_{15}$	$FeNa_2^*C_{10}H_8$
$F_{15}Hg_5NO_{12}^*C_{16}$	$FeO^*C_{12}H_{14}$
$F_{15}Hg_5O_{10}^*C_{16}H$	$FeO_2^*C_{10}H_{10}BCl$
$F_{15}Hg_5O_{10}^*C_{17}H_3$	$FeO_2^*C_{10}H_{11}B$
$F_{15}Li^*C_7$	$FeO_2^*C_{15}H_{14}$
$F_{15}LiPb^*C_{18}$	$FeSn^*C_{30}H_{26}$
$F_{15}N^*C_{44}H_{36}AuBr$	$Fe_2HgN_2^*C_{28}H_{36}$

$\text{Ge}^*\text{Au}_2$   
 $\text{Ge}^*\text{CH}_6$   
 $\text{Ge}^*\text{C}_2\text{H}_8$   
 $\text{Ge}^*\text{C}_3\text{H}_9\text{Br}$   
 $\text{Ge}^*\text{C}_3\text{H}_9\text{Cl}$   
 $\text{Ge}^*\text{C}_6\text{H}_5\text{Cl}$   
 $\text{Ge}^*\text{C}_6\text{H}_{15}\text{Br}$   
 $\text{Ge}^*\text{C}_6\text{H}_{15}\text{Cl}$   
 $\text{Ge}^*\text{C}_6\text{H}_{15}\text{Cs}$   
 $\text{Ge}^*\text{C}_6\text{H}_{16}$   
 $\text{Ge}^*\text{C}_7\text{H}_{18}$   
 $\text{Ge}^*\text{C}_8\text{H}_{11}\text{Cl}$   
 $\text{Ge}^*\text{C}_8\text{H}_{18}\text{Cl}_2$   
 $\text{Ge}^*\text{C}_8\text{H}_{20}$   
 $\text{Ge}^*\text{C}_{12}\text{HBrF}_{10}$   
 $\text{Ge}^*\text{C}_{12}\text{H}_{10}\text{Br}_2$   
 $\text{Ge}^*\text{C}_{12}\text{H}_{12}$   
 $\text{Ge}^*\text{C}_{12}\text{H}_{19}\text{Br}$   
 $\text{Ge}^*\text{C}_{12}\text{H}_{20}$   
 $\text{Ge}^*\text{C}_{12}\text{H}_{28}$   
 $\text{Ge}^*\text{C}_{16}\text{H}_{36}$   
 $\text{Ge}^*\text{C}_{17}\text{H}_{16}$   
 $\text{Ge}^*\text{C}_{18}\text{BrF}_{15}$   
 $\text{Ge}^*\text{C}_{18}\text{ClF}_{15}$   
 $\text{Ge}^*\text{C}_{18}\text{HF}_{15}$   
 $\text{Ge}^*\text{C}_{18}\text{H}_{15}\text{Br}$   
 $\text{Ge}^*\text{C}_{18}\text{H}_{15}\text{Cl}$   
 $\text{Ge}^*\text{C}_{18}\text{H}_{15}\text{F}$   
 $\text{Ge}^*\text{C}_{18}\text{H}_{16}$   
 $\text{Ge}^*\text{C}_{18}\text{H}_{18}$   
 $\text{Ge}^*\text{C}_{19}\text{H}_{20}$   
 $\text{Ge}^*\text{C}_{20}\text{H}_{18}$   
 $\text{Ge}^*\text{C}_{21}\text{H}_{22}$   
 $\text{Ge}^*\text{C}_{24}\text{F}_{20}$   
 $\text{Ge}^*\text{C}_{24}\text{H}_{20}$   
 $\text{Ge}^*\text{C}_{26}\text{H}_{24}$   
 $\text{Ge}^*\text{C}_{28}\text{H}_{28}$   
 $\text{Ge}^*\text{C}_{34}\text{H}_{26}$   
 $\text{Ge}^*\text{C}_{37}\text{H}_{30}$   
 $\text{Ge}^*\text{C}_{72}\text{H}_{60}\text{Ag}$   
 $\text{Ge}^*\text{Cl}_4$   
 $\text{Ge}^*\text{Cs}$   
 $\text{Ge}^*\text{Cu}_3$   
 $\text{Ge}^*\text{F}_2$   
 $\text{GeH}^*\text{Cl}_3$   
 $\text{GeH}_3^*\text{Br}$   
 $\text{GeH}_3^*\text{Cs}$   
 $\text{GeH}_3\text{K}$

$\text{K}[\text{GeH}_3]$

Formation: 5.5.5, 5.5.5.4

$\text{GeH}_3\text{Na}$

$\text{Na}[\text{GeH}_3]$

Formation: 5.5.5.4, 5.5.5.4

$\text{GeH}_3\text{Rb}$

$\text{Rb}[\text{GeH}_3]$

Formation: 5.5.5.4

$\text{GeH}_4$

$\text{GeH}_4$

Reaction with  $\text{K}[\text{NH}_2]$ : 5.5.5.4

Reaction with Li, K, Na, Rb or Cs metal: 5.5.5.4

$\text{GeHg}^*\text{C}_8\text{H}_{20}$

$\text{GeHg}^*\text{C}_8\text{H}_{26}\text{B}_{10}$

$\text{GeHg}^*\text{C}_{20}\text{H}_5\text{F}_{15}$

$\text{GeHgN}^*\text{C}_{10}\text{H}_{21}$

$\text{GeHgN}_2^*\text{C}_{13}\text{H}_{24}$

$\text{GeHgSi}^*\text{C}_3\text{H}_9\text{Cl}_3$

$\text{GeHgSi}^*\text{C}_4\text{H}_{11}\text{Cl}_3$

$\text{GeHgSi}^*\text{C}_6\text{H}_{18}$

$\text{GeHgSi}^*\text{C}_{12}\text{H}_{30}$

$\text{GeHgSn}^*\text{C}_{36}\text{F}_{30}$

$\text{GeI}_2$

$\text{GeI}_2$

Reaction with  $\text{R}_3\text{GeLi}$ : 5.5.5.7

$\text{GeK}$

$\text{KGe}$

Formation: 5.5.5.1

$\text{GeK}^*\text{C}_6\text{H}_{15}$

$\text{GeK}^*\text{C}_{18}\text{H}_{15}$

$\text{GeK}_2^*\text{C}_8\text{H}_{18}$

$\text{GeLi}^*\text{C}_2\text{H}_7$

$\text{GeLi}^*\text{C}_3\text{H}_9$

$\text{GeLi}^*\text{C}_6\text{H}_7$

$\text{GeLi}^*\text{C}_6\text{H}_9$

$\text{GeLi}^*\text{C}_6\text{H}_{15}$

$\text{GeLi}^*\text{C}_7\text{H}_{17}$

$\text{GeLi}^*\text{C}_8\text{H}_{11}$

$\text{GeLi}^*\text{C}_9\text{H}_{21}$

$\text{GeLi}^*\text{C}_{12}\text{H}_{11}$

$\text{GeLi}^*\text{C}_{12}\text{H}_{19}$

$\text{GeLi}^*\text{C}_{18}\text{F}_{15}$

$\text{GeLi}^*\text{C}_{18}\text{H}_{15}$

$\text{GeLi}^*\text{C}_{19}\text{H}_{17}$

$\text{GeLi}^*\text{C}_{20}\text{H}_{19}$

$\text{GeLi}^*\text{C}_{21}\text{H}_{21}$

$\text{GeLi}^*\text{C}_{26}\text{H}_{23}$

$\text{GeLiOS}^*\text{C}_7\text{H}_{15}$

$\text{GeLiPb}^*\text{C}_{37}\text{H}_{31}$

$\text{GeLiSi}_3^*\text{C}_{12}\text{H}_{33}$

$\text{GeLi}_2^*\text{C}_{12}\text{H}_{10}$

$\text{GeLi}_2^*\text{C}_{14}\text{H}_{14}$

$\text{GeLi}_4$

$\text{Li}_4\text{Ge}$

Formation: 5.5.5.1, 5.5.5.3

$\text{GeN}_3\text{Na}^*\text{C}_{18}\text{H}_{24}$

**GeNa**

NaGe

Formation: 5.5.5.1

$\text{GeNa} \cdot \text{CH}_5$   
 $\text{GeNa} \cdot \text{C}_2\text{H}_7$   
 $\text{GeNa} \cdot \text{C}_6\text{H}_{15}$   
 $\text{GeNa} \cdot \text{C}_{12}\text{H}_{27}$   
 $\text{GeNa} \cdot \text{C}_{18}\text{H}_{15}$   
 $\text{GeNa}_2 \cdot \text{C}_{12}\text{H}_{10}$   
 $\text{GeO} \cdot \text{C}_4\text{H}_{12}$   
 $\text{GeO} \cdot \text{C}_8\text{H}_{20}$   
 $\text{GeOS} \cdot \text{C}_7\text{H}_{16}$   
 $\text{GeO}_3 \cdot \text{C}_{21}\text{H}_{22}$   
 $\text{GeO}_3\text{Zn} \cdot \text{C}_{26}\text{H}_{34}$   
 $\text{GeP} \cdot \text{C}_{21}\text{H}_{24}\text{Au}$   
 $\text{GeP} \cdot \text{C}_{36}\text{H}_{30}\text{Au}$   
 $\text{GeP}_2 \cdot \text{C}_{44}\text{H}_{39}\text{Au}$   
 $\text{GeP}_3 \cdot \text{C}_{72}\text{H}_{60}\text{Cu}$   
 $\text{GePb} \cdot \text{C}_{37}\text{H}_{30}\text{Cl}_2$   
 $\text{GePb} \cdot \text{C}_{37}\text{H}_{32}$   
 $\text{GePb}_2 \cdot \text{C}_{55}\text{H}_{46}$

**GeRb**

RbGe

Formation: 5.5.5.1

$\text{GeSi} \cdot \text{C}_{24}\text{H}_{30}$   
 $\text{Ge}_2 \cdot \text{Au}$   
 $\text{Ge}_2 \cdot \text{C}_{12}\text{H}_{14}$   
 $\text{Ge}_2 \cdot \text{C}_{12}\text{H}_{18}$   
 $\text{Ge}_2 \cdot \text{C}_{12}\text{H}_{30}$   
 $\text{Ge}_2 \cdot \text{C}_{12}\text{H}_{30}\text{Cd}$   
 $\text{Ge}_2 \cdot \text{C}_{18}\text{H}_{42}$   
 $\text{Ge}_2 \cdot \text{C}_{24}\text{Br}_2\text{F}_{20}$   
 $\text{Ge}_2 \cdot \text{C}_{24}\text{H}_{15}\text{F}_{15}$   
 $\text{Ge}_2 \cdot \text{C}_{24}\text{H}_{20}\text{Br}_2$   
 $\text{Ge}_2 \cdot \text{C}_{24}\text{H}_{22}$   
 $\text{Ge}_2 \cdot \text{C}_{24}\text{H}_{38}$   
 $\text{Ge}_2 \cdot \text{C}_{36}\text{CdF}_{30}$   
 $\text{Ge}_2 \cdot \text{C}_{36}\text{F}_{30}$   
 $\text{Ge}_2 \cdot \text{C}_{36}\text{H}_{30}$   
 $\text{Ge}_2 \cdot \text{C}_{36}\text{H}_{30}\text{Cd}$   
 $\text{Ge}_2 \cdot \text{C}_{38}\text{H}_5\text{BiF}_{30}$   
 $\text{Ge}_2 \cdot \text{Cl}_6$

 **$\text{Ge}_2\text{H}_6\text{Hg}$**  $(\text{H}_3\text{Ge})_2\text{Hg}$ 

Formation: 5.7.4

$\text{Ge}_2\text{Hg} \cdot \text{C}_3\text{H}_{12}$   
 $\text{Ge}_2\text{Hg} \cdot \text{C}_6\text{H}_{18}$   
 $\text{Ge}_2\text{Hg} \cdot \text{C}_{12}\text{H}_{30}$   
 $\text{Ge}_2\text{Hg} \cdot \text{C}_{18}\text{H}_{42}$   
 $\text{Ge}_2\text{Hg} \cdot \text{C}_{24}\text{H}_{15}\text{F}_{15}$   
 $\text{Ge}_2\text{Hg} \cdot \text{C}_{34}\text{H}_{30}$   
 $\text{Ge}_2\text{Hg} \cdot \text{C}_{36}\text{F}_{30}$

$\text{Ge}_2\text{Hg} \cdot \text{C}_{36}\text{H}_{30}$   
 $\text{Ge}_2\text{Hg} \cdot \text{Cl}_6$   
 $\text{Ge}_2\text{HgP}_2\text{Pd} \cdot \text{C}_{72}\text{H}_{60}$   
 $\text{Ge}_2\text{HgSi}_2 \cdot \text{C}_8\text{H}_{22}$   
 $\text{Ge}_2\text{HgSi}_6 \cdot \text{C}_{24}\text{H}_{66}$   
 $\text{Ge}_2\text{Li} \cdot \text{C}_{36}\text{H}_{30}\text{Au}$   
 $\text{Ge}_2\text{Li}_2 \cdot \text{C}_{24}\text{H}_{20}$

 **$\text{Ge}_2\text{Li}_6$**  $\text{Li}_6\text{Ge}_2$ 

Formation: 5.5.5.1

$\text{Ge}_2\text{O}_2\text{Zn} \cdot \text{C}_{44}\text{H}_{20}\text{F}_{30}$   
 $\text{Ge}_2\text{O}_3\text{Zn} \cdot \text{C}_{42}\text{H}_{44}$   
 $\text{Ge}_2\text{P}_2 \cdot \text{C}_{72}\text{H}_{30}\text{CdF}_{30}$   
 $\text{Ge}_2\text{P}_2\text{Pd} \cdot \text{C}_{72}\text{H}_{60}\text{Cd}$   
 $\text{Ge}_2\text{Zn} \cdot \text{C}_{36}\text{F}_{30}$   
 $\text{Ge}_2\text{Zn} \cdot \text{C}_{36}\text{H}_{30}$   
 $\text{Ge}_3 \cdot \text{C}_{36}\text{H}_{30}\text{F}_2$   
 $\text{Ge}_3 \cdot \text{C}_{42}\text{H}_{35}\text{Cl}$   
 $\text{Ge}_3\text{Hg} \cdot \text{C}_{36}\text{H}_{30}\text{F}_2$   
 $\text{Ge}_3\text{Hg} \cdot \text{C}_{42}\text{H}_{35}\text{Cl}$   
 $\text{Ge}_3\text{LiSi} \cdot \text{C}_{54}\text{H}_{45}$   
 $\text{Ge}_3\text{Si} \cdot \text{C}_{54}\text{H}_{46}$   
 $\text{Ge}_3\text{Si}_3\text{Ti} \cdot \text{C}_{12}\text{H}_{33}$   
 $\text{Ge}_3\text{Ti} \cdot \text{C}_{18}\text{H}_{45}$   
 $\text{Ge}_4 \cdot \text{C}_{48}\text{H}_{40}$   
 $\text{Ge}_4 \cdot \text{C}_{54}\text{H}_{46}$   
 $\text{Ge}_4\text{Li} \cdot \text{C}_{54}\text{H}_{45}$   
 $\text{Ge}_5 \cdot \text{C}_{60}\text{H}_{50}$   
 $\text{Ge}_5\text{HgPr} \cdot \text{C}_{90}\text{F}_{75}$   
 $\text{HBrCili} \cdot \text{C}$   
 $\text{HBrF}_{10}\text{Ge} \cdot \text{C}_{12}$   
 $\text{HBr}_2\text{Li} \cdot \text{C}$   
 $\text{HBr}_2\text{Na} \cdot \text{C}$   
 $\text{HCl}_2\text{Li} \cdot \text{C}$   
 $\text{HCl}_2\text{Li} \cdot \text{C}_2$   
 $\text{H} \cdot \text{Cl}_3\text{Ge}$   
 $\text{PPHCl}_3\text{Hg}_3 \cdot \text{C}$   
 $\text{HCl}_4\text{Li} \cdot \text{C}_6$   
 $\text{HF}_2\text{Li} \cdot \text{C}_2$   
 $\text{HF}_{15}\text{Ge} \cdot \text{C}_{18}$   
 $\text{HF}_{15}\text{Hg}_5\text{O}_{10} \cdot \text{C}_{16}$   
 $\text{HF}_{15}\text{Sn} \cdot \text{C}_{18}$   
 $\text{HILiNS} \cdot \text{C}_3$

**HK**

KH

Base for metallation reaction: 5.5.3.3.1

Deprotonation of SiH: 5.5.4.4

Reaction with disilanes: 5.5.4.2.2

**HKO**

KOH

Electrolyte: 5.5.7.1.3

Reaction with disilanes: 5.5.4.2.2



- HLi**\*C<sub>2</sub>  
**HLiO**  
 LiOH  
     Electrolyte: 5.5.7.1.3  
     Reaction with LiH and Pb: 5.5.7.1.2  
**HLi<sub>2</sub>N**\*C<sub>2</sub>  
**HLi<sub>3</sub>**\*C<sub>3</sub>  
**HNa**  
 NaH  
     Base for metallation reaction: 5.5.3.3.1  
     Deprotonation of SiH: 5.5.4.4  
     Reaction with Pb metal: 5.5.7.1.2  
**HNa**\*C<sub>2</sub>  
**HNaO**  
 NaOH  
     Electrolyte: 5.5.7.1.3  
     Reaction with NaH and Pb: 5.5.7.1.2  
**HSi**\*Cl<sub>3</sub>  
**H<sub>2</sub>AuK**\*C<sub>4</sub>  
**H<sub>2</sub>BrClHg**\*C<sub>2</sub>  
**H<sub>2</sub>BrCl<sub>3</sub>Hg**\*C<sub>2</sub>  
**H<sub>2</sub>BrLi**\*C  
**H<sub>2</sub>BrLiO**\*C<sub>4</sub>  
**H<sub>2</sub>BrLiS**\*C<sub>4</sub>  
**H<sub>2</sub>ClHgN**\*C<sub>2</sub>  
**H<sub>2</sub>ClHgNS**\*C<sub>3</sub>  
**H<sub>2</sub>ClLi**\*C  
**H<sub>2</sub>ClLi**\*C<sub>2</sub>  
**H<sub>2</sub>ClLiS**\*C<sub>4</sub>  
**H<sub>2</sub>Cl<sub>2</sub>F<sub>6</sub>Hg**\*C<sub>4</sub>  
**H<sub>2</sub>Cl<sub>2</sub>Hg**\*C<sub>2</sub>  
**H<sub>2</sub>Cl<sub>2</sub>HgO**\*C<sub>2</sub>  
**H<sub>2</sub>Cl<sub>2</sub>Hg<sub>2</sub>**\*C  
**H<sub>2</sub>Cl<sub>2</sub>Hg<sub>2</sub>O**\*C<sub>4</sub>  
**H<sub>2</sub>Cl<sub>2</sub>Hg<sub>2</sub>S**\*C<sub>4</sub>  
**H<sub>2</sub>Cl<sub>3</sub>Li**\*C<sub>6</sub>  
**H<sub>2</sub>Cl<sub>8</sub>Hg**\*C<sub>12</sub>  
**H<sub>2</sub>Cl<sub>12</sub>Hg<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**\*C<sub>18</sub>  
**H<sub>2</sub>CuNO<sub>2</sub>**\*C<sub>3</sub>  
**H<sub>2</sub>DBrMg**\*C  
**H<sub>2</sub>FLiS**\*C<sub>4</sub>  
**H<sub>2</sub>F<sub>3</sub>Li**\*C<sub>3</sub>  
**H<sub>2</sub>F<sub>8</sub>Hg**\*C<sub>12</sub>  
**H<sub>2</sub>F<sub>8</sub>HgO<sub>3</sub>S**\*C<sub>12</sub>  
**H<sub>2</sub>F<sub>12</sub>Hg**\*C<sub>6</sub>  
**H<sub>2</sub>F<sub>12</sub>Hg<sub>2</sub>O<sub>6</sub>S<sub>2</sub>**\*C<sub>18</sub>  
**H<sub>2</sub>F<sub>16</sub>Hg**\*C<sub>8</sub>  
**H<sub>2</sub>HgI<sub>2</sub>**\*C  
**H<sub>2</sub>HgN**\*Cl  
**H<sub>2</sub>HgN<sub>4</sub>**\*C<sub>6</sub>  
**H<sub>2</sub>Hg<sub>2</sub>I<sub>3</sub>**\*C  
**H<sub>2</sub>ILiS**\*C<sub>4</sub>  
**H<sub>2</sub>I<sub>2</sub>Zn**\*C  
**H<sub>2</sub>I<sub>2</sub>Zn<sub>2</sub>**\*C  
**H<sub>2</sub>LiN**\*C<sub>2</sub>  
**H<sub>2</sub>LiNS**\*C<sub>3</sub>  
**H<sub>2</sub>LiNSE**\*C<sub>5</sub>  
**H<sub>2</sub>Li<sub>2</sub>**\*C  
**H<sub>2</sub>Li<sub>2</sub>**\*C<sub>3</sub>  
**H<sub>2</sub>Li<sub>2</sub>OS**\*C<sub>2</sub>  
**H<sub>2</sub>Li<sub>2</sub>O<sub>2</sub>**\*C<sub>4</sub>  
**H<sub>2</sub>Li<sub>2</sub>O<sub>3</sub>**\*C<sub>5</sub>  
**H<sub>2</sub>Li<sub>3</sub>S**\*C<sub>4</sub>  
**H<sub>2</sub>NNa**  
 Na[NH<sub>2</sub>]  
     Base for metallation reaction: 5.5.3.3.1  
**H<sub>2</sub>N<sub>2</sub>**\*C  
**H<sub>2</sub>NaS**\*C<sub>4</sub>  
**H<sub>2</sub>Na<sub>2</sub>Sn**  
 Na<sub>2</sub>[SnH<sub>2</sub>]  
     Formation: 5.5.6.4  
**H<sub>3</sub>AgF<sub>7</sub>N**\*C<sub>5</sub>  
**H<sub>3</sub>Ag<sub>2</sub>NO<sub>3</sub>**\*C  
**H<sub>3</sub>**\*B  
**H<sub>3</sub>BrCd**\*C<sub>4</sub>  
**H<sub>3</sub>BrCl<sub>2</sub>Hg**\*C<sub>6</sub>  
**H<sub>3</sub>BrCl<sub>2</sub>Mg**\*C<sub>6</sub>  
**H<sub>3</sub>**\*BrGe  
**H<sub>3</sub>BrHg**\*C  
**H<sub>3</sub>BrHg**\*C<sub>2</sub>  
**H<sub>3</sub>BrLiN**\*C<sub>5</sub>  
**H<sub>3</sub>BrLi<sub>2</sub>**\*C  
**H<sub>3</sub>BrMg**\*C  
**H<sub>3</sub>BrMg**\*C<sub>2</sub>  
**H<sub>3</sub>BrMg**\*C<sub>3</sub>  
**H<sub>3</sub>BrMg**\*C<sub>4</sub>  
**H<sub>3</sub>BrZn**\*C<sub>3</sub>  
**H<sub>3</sub>CdCl**\*C  
**H<sub>3</sub>CdI**\*C  
**H<sub>3</sub>ClF<sub>4</sub>HgO**\*C<sub>7</sub>  
**H<sub>3</sub>ClHg**\*C  
**H<sub>3</sub>ClHg**\*C<sub>2</sub>  
**H<sub>3</sub>ClHg**\*C<sub>3</sub>  
**H<sub>3</sub>ClHgO**\*C<sub>4</sub>  
**H<sub>3</sub>ClHgS**\*C<sub>4</sub>  
**H<sub>3</sub>ClLiN**\*C<sub>7</sub>  
**H<sub>3</sub>ClOZn**\*C  
**H<sub>3</sub>ClS**\*C<sub>4</sub>  
**H<sub>3</sub>Cl<sub>2</sub>F<sub>3</sub>Hg<sub>2</sub>**\*C<sub>7</sub>  
**H<sub>3</sub>Cl<sub>2</sub>Li**\*C<sub>2</sub>  
**H<sub>3</sub>Cl<sub>2</sub>Li**\*C<sub>3</sub>  
**H<sub>3</sub>Cl<sub>3</sub>Hg**\*C<sub>3</sub>  
**H<sub>3</sub>Cl<sub>3</sub>Hg**\*C<sub>6</sub>  
**H<sub>3</sub>**\*CsGe

$H_3D_2HgN^*C_3$	$H_4ClHg^*C_5$
$H_3FHg^*C$	$H_4ClHgMnO_3^*C_8$
$H_3F_2Li^*C_3$	$H_4ClHgNO_2^*C_6$
$H_3F_5Hg^*C_7$	$H_4ClHgO_3Re^*C_8$
$H_3F_5HgO_2^*C_8$	$H_4ClLi^*C_3$
$H_3F_6HgNO_2^*C_5$	$H_4ClLi^*C_6$
$H_3F_6Li^*C_8$	$H_4ClLiO^*C_4$
$H_3F_{15}Hg_5O_{10}^*C_{17}$	$H_4Cl_2Hg^*C_2$
$H_3HgI^*C$	$H_4Cl_2Hg^*C_3$
$H_3IMg^*C$	$H_4Cl_2Hg^*C_4$
$H_3K^*C$	$H_4Cl_2Hg^*C_6$
$H_3K^*Ge$	$H_4Cl_2HgO_2S^*C_6$
$H_3KO^*C$	$H_4Cl_2Si^*C$
<b><math>H_3KSi</math></b>	$H_4Cl_2Zn^*C_2$
$K[SiH_3]$	$H_4Cl_3Sb^*C_6$
Formation: 5.5.3.3.3, 5.5.4.4	$H_4Cl_6Hg^*C_{12}$
$H_3Li^*C$	$H_4Cl_{10}HgO_8S_2^*C_{12}$
$H_3Li^*C_2$	$H_4CuF_3^*C_7$
$H_3Li^*C_3$	$H_4CuMnO_3^*C_8$
$H_3LiN_2O^*C_3$	$H_4D_2Zn^*C_2$
$H_3LiN_4^*C_2$	$H_4FLi^*C_6$
$H_3LiO^*C_4$	$H_4F_3Li^*C_7$
$H_3LiS^*C_4$	$H_4F_6Li_2O^*C_9$
$H_3LiS_2^*C_4$	$H_4F_{10}HgO_8S_2^*C_{12}$
$H_3LiS_4^*C_6$	$H_4^*Ge$
$H_3LiSe^*C_4$	$H_4HgINO_2^*C_6$
$H_3Li_2N^*C_5$	$H_4HgN_2^*C_4$
$H_3Li_3^*C_4$	$H_4HgN_6O_{12}^*C_4$
$H_3Li_3^*C_5$	$H_4HgN_6O_{12}^*C_{12}$
$H_3Li_3O_4^*C_4$	$H_4HgN_6O_{16}^*C_{14}$
$H_3N$	$H_4I_2Zn^*C_2$
$NH_3$	$H_4KLiO^*C_3$
Solvent: 5.5.7.3	$H_4LiN^*C_3$
$H_3Na^*C$	$H_4LiN^*C_4$
$H_3Na^*Ge$	$H_4LiN^*C_5$
$H_3NaO^*C$	$H_4LiN^*C_7$
<b><math>H_3NaSn</math></b>	$H_4LiNO^*C_4$
$Na[SnH_3]$	$H_4LiNO_2^*C_6$
Formation: 5.5.6.4	$H_4LiO_3Re^*C_8$
NMR: 5.5.6.4	$H_4Li_2^*C_2$
$H_3Rb^*Ge$	$H_4Li_2^*C_6$
$H_3Si^*Br$	$H_4Li_2NO_2^*C_2$
$H_3Si^*Cl$	$H_4Li_2NO_2^*C_3$
$H_4AgMnO_3^*C_8$	$H_4Li_2O^*C_3$
$H_4BrClMg^*C_6$	$H_4Li_2O^*C_6$
$H_4BrHgMnO_3^*C_8$	$H_4Li_2O_2^*C_3$
$H_4BrHgNO_2^*C_6$	$H_4Li_2O_2^*C_4$
$H_4BrHgO_3Re^*C_8$	$H_4Li_2O_2^*C_7$
$H_4BrLi^*C_6$	$H_4Li_2O_3S^*C_6$
$H_4CdI_2^*C_2$	$H_4Li_2S^*C_3$
$H_4ClCu^*C_6$	$H_4Li_2S^*C_6$
$H_4ClF_3Hg^*C_7$	$H_4Li_3N^*C_6$

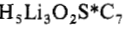
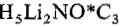
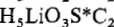
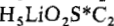
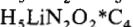
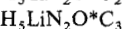
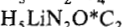
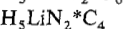
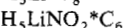
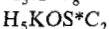
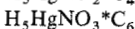
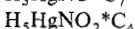
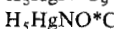
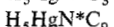
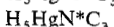
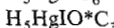
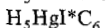
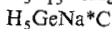
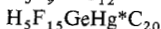
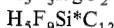
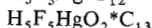
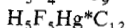
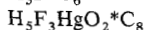
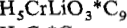
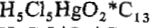
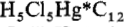
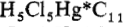
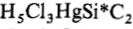
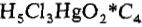
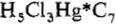
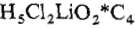
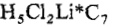
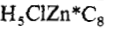
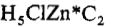
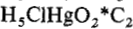
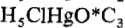
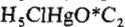
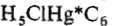
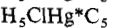
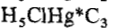
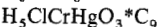
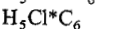
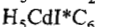
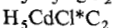
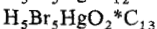
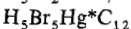
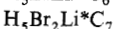
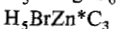
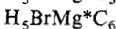
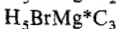
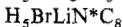
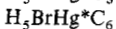
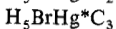
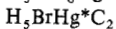
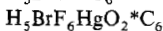
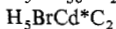
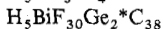
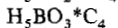
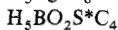


Formation: 5.5.4.3

Reaction with Na or K metal: 5.5.4.4



Reaction with Na metal: 5.5.6.4



$H_5Na^*C_8$	$H_6HgO_2^*C_4$
$H_5NaOS^*C_2$	$H_6HgO_2^*C_5$
$H_5NaSn^*C$	$H_6HgO_4^*C_4$
$H_5Rb^*C_3$	$H_6HgSi^*C_2$
$H_5Tl^*C_3$	<b><math>H_6HgSi_2</math></b>
$H_6AuLi^*C_2$	$(H_3Si)_2Hg$
$H_6BMnO_5^*C_8$	Formation: 5.7.3
$H_6BO_3Re^*C_8$	$H_6Hg_2^*C_4$
$H_6^*B_2$	$H_6Hg_2O^*C_2$
$H_6BrLi^*C_5$	$H_6I_4Zn_2^*C_8$
$H_6BrLi^*C_{10}$	$H_6K^*C_6$
$H_6BrLiO^*C_4$	$H_6Li^*C_6$
$H_6Br_2Hg_2^*C_3$	$H_6LiN^*C_4$
$H_6Br_8HgO_2^*C_{14}$	$H_6LiN^*C_6$
$H_6Br_8HgO_6^*C_{16}$	$H_6LiN^*C_8$
$H_6^*C_6$	$H_6LiN^*C_9$
$H_6Cd^*C_2$	$H_6LiNO^*C_3$
$H_6Cd^*C_3$	$H_6LiNO_2^*C_4$
$H_6ClHgNO_2S^*C_6$	$H_6LiNO_2^*C_7$
$H_6ClHgNO_3^*C_8$	$H_6LiNS^*C_3$
$H_6ClHgNO_6^*C_3$	$H_6LiNS^*C_5$
$H_6ClLi^*C_4$	$H_6LiNS^*C_8$
$H_6ClLi^*C_8$	$H_6LiNS_2^*C_4$
$H_6ClLiO^*C_4$	$H_6LiNS_2^*C_5$
$H_6ClLiOS^*C_7$	$H_6LiN_3^*C_8$
$H_6Cl_2HgO_2^*C_8$	$H_6Li_2^*C_4$
$H_6Cl_2Mg^*C_7$	$H_6Li_2^*C_5$
$H_6Cl_2Pb^*C_2$	$H_6Li_2^*C_7$
$H_6Cl_4Hg^*C_{12}$	$H_6Li_2^*C_9$
$H_6Cl_4HgSi_2^*C_2$	$H_6Li_2^*C_{10}$
$H_6Cl_8HgO_8S_2^*C_{12}$	$H_6Li_2^*C_{12}$
$H_6CrO_3^*C_9$	$H_6Li_2O^*C_3$
$H_6Cs^*C_6$	$H_6Li_2O^*C_7$
$H_6CuLi^*C_2$	$H_6Li_2O_2^*C_4$
$H_6FLi^*C_7$	$H_6Li_2O_2^*C_5$
$H_6FLiO^*C_7$	$H_6Li_2O_2^*C_8$
$H_6F_3LiSe^*C_8$	$H_6Li_2O_2^*C_9$
$H_6F_3LiSe^*C_9$	$H_6Li_2O_2S^*C_7$
$H_6F_4Hg^*C_{12}$	$H_6Li_2O_2S^*C_8$
$H_6F_4HgO_4^*C_{14}$	$H_6Li_2O_2Se^*C_8$
$H_6F_4Hg_2O_2^*C_{10}$	$H_6Li_2O_3^*C_8$
$H_6F_8HgO_2^*C_{14}$	$H_6Li_2S^*C_7$
$H_6F_8HgO_8S_2^*C_{12}$	$H_6Li_2S^*C_9$
$H_6Ge^*C$	$H_6Li_2Se^*C_9$
$H_6Hg^*C_2$	$H_6Na_2Sn^*C_2$
$H_6Hg^*C_3$	$H_6O_2^*C_4$
$H_6Hg^*C_4$	$H_6O_2S^*C_4$
$H_6Hg^*C_6$	$H_6O_2Zn^*C_2$
$H_6Hg^*C_{10}$	$H_6Rb^*C_6$
$H_6Hg^*Ge_2$	$H_6Sn^*C_2$
$H_6HgN_2O^*C_4$	$H_6Zn^*C_2$
$H_6HgN_2O_2^*C_4$	$H_6Zn^*C_4$

$H_6Zn^*C_6$	$H_7Li^*C_3$
$H_7Ag^*C_8$	$H_7Li^*C_4$
$H_7BCrO_5^*C_9$	$H_7Li^*C_5$
$H_7BO_2^*C_6$	$H_7Li^*C_6$
$H_7BrHg^*C_7$	$H_7Li^*C_7$
$H_7BrHg^*C_8$	$H_7Li^*C_8$
$H_7BrHg^*C_{10}$	$H_7Li^*C_9$
$H_7BrHgO^*C_7$	$H_7Li^*C_{10}$
$H_7BrHgO_2^*C_8$	$H_7LiN_2^*C_5$
$H_7BrMg^*C_3$	$H_7LiN_2^*C_7$
$H_7BrMg^*C_4$	$H_7LiN_2^*C_9$
$H_7BrMg^*C_7$	$H_7LiN_2O^*C_4$
$H_7BrZn^*C_7$	$H_7LiO^*C_3$
$H_7CdCl^*C_3$	$H_7LiO^*C_4$
$H_7ClHg^*C_3$	$H_7LiO^*C_5$
$H_7ClHg^*C_5$	$H_7LiO^*C_7$
$H_7ClHg^*C_7$	$H_7LiO^*C_8$
$H_7ClHgO^*C_9$	$H_7LiOS^*C_4$
$H_7ClHgO_2^*C_3$	$H_7LiOS^*C_5$
$H_7ClHgO_2^*C_5$	$H_7LiOS^*C_7$
$H_7ClHgO_2^*C_8$	$H_7LiOS_2^*C_3$
$H_7ClHgO_2S^*C_7$	$H_7LiOS_2^*C_4$
$H_7ClHgO_5^*C_3$	$H_7LiOSE^*C_7$
$H_7ClMg^*C_3$	$H_7LiO_2^*C_4$
$H_7ClMg^*C_4$	$H_7LiO_2S^*C_7$
$H_7ClMg^*C_7$	$H_7LiO_3S^*C_4$
$H_7ClSi^*C_2$	$H_7LiO_3S^*C_8$
$H_7ClZn^*C_4$	$H_7LiS^*C_4$
$H_7ClZn^*C_7$	$H_7LiS^*C_5$
$H_7ClZn^*C_{10}$	$H_7LiS^*C_7$
$H_7Cl_4NSi^*C_7$	$H_7LiS^*C_8$
$H_7Cl_5Hg^*C_{13}$	$H_7LiS_2^*C_3$
$H_7Cl_5HgO_2^*C_{14}$	$H_7LiS_2^*C_4$
$H_7Cl_5Si^*C_8$	$H_7LiS_4^*C_4$
$H_7Cs^*C_7$	$H_7LiSe^*C_7$
$H_7Cu^*C_7$	$H_7LiSe^*C_8$
$H_7CuO^*C_7$	$H_7LiTe^*C_7$
$H_7D_2Li^*C_5$	$H_7Li_2N^*C_{10}$
$H_7F_3Si^*C_8$	$H_7Li_2NO^*C_8$
$H_7GeLi^*C_2$	$H_7Li_2NO^*C_9$
$H_7GeLi^*C_6$	$H_7Li_2NO_2S^*C_3$
$H_7GeNa^*C_2$	$H_7Li_2NO_2S^*C_9$
$H_7HgI^*C_7$	$H_7Li_2NS^*C_8$
$H_7HgIO^*C_4$	$H_7Li_3^*C_7$
$H_7HgIO^*C_8$	$H_7Li_3^*C_8$
$H_7HgNO^*C_8$	$H_7Na^*C_7$
$H_7HgNO_4^*C_8$	$H_7NaO^*C_8$
$H_7IZn^*C_7$	$H_7NaSn^*C_2$
$H_7K^*C_3$	$H_7NaSn^*C_6$
$H_7K^*C_5$	$H_7O_2Ti^*C_4$
$H_7K^*C_7$	$H_8AgClFe^*C_{10}$
$H_7KO^*C_5$	$H_8AgCuMnO_6^*C_{16}$

$H_8BClHgO_2 \cdot C_3$	$H_8LiNO_2S \cdot C_3$
$H_8BNO_5 \cdot C_8$	$H_8LiNS \cdot C_5$
$H_8BrHgLiO \cdot C_8$	$H_8LiNS \cdot C_8$
$H_8BrLi \cdot C_8$	$H_8LiNS_2 \cdot C_4$
$H_8BrLiO \cdot C_5$	$H_8LiN_3 \cdot C_{10}$
$H_8BrLiO_2S \cdot C_{12}$	$H_8LiO_2PS \cdot C_3$
$H_8Br_2Zn_2 \cdot C_4$	$H_8LiO_3P \cdot C_3$
$H_8 \cdot C_5$	$H_8LiP \cdot C_3$
$H_8 \cdot C_6$	$H_8Li_2 \cdot C_4$
$H_8CdCl_2 \cdot C_{12}$	$H_8Li_2 \cdot C_8$
$H_8ClLi \cdot C_7$	$H_8Li_2 \cdot C_9$
$H_8ClLiO \cdot C_{12}$	$H_8Li_2 \cdot C_{10}$
$H_8ClLiO_2 \cdot C_6$	$H_8Li_2 \cdot C_{12}$
$H_8ClNaO_2 \cdot C_5$	$H_8Li_2N_2 \cdot C_9$
$H_8Cl_2FeHg \cdot C_{10}$	$H_8Li_2O \cdot C_8$
$H_8Cl_2FeHg_2 \cdot C_{10}$	$H_8Li_2O \cdot C_{10}$
$H_8Cl_2Hg \cdot C_4$	$H_8Li_2O \cdot C_{12}$
$H_8Cl_2Hg \cdot C_{12}$	$H_8Li_2O_2 \cdot C_9$
$H_8Cl_2HgO_2S \cdot C_{12}$	$H_8Li_2O_2S \cdot C_{12}$
$H_8Cl_2Hg_2O \cdot C_4$	$H_8Li_2O_3S \cdot C_9$
$H_8Cl_2Hg_2O_2 \cdot C_4$	$H_8Li_2S \cdot C_{12}$
$H_8Cl_2Zn \cdot C_{12}$	$H_8Li_2S_2 \cdot C_6$
$H_8D_2HgO_3 \cdot C_5$	$H_8Li_3 \cdot C_6$
$H_8FLi \cdot C_9$	$H_8N_3Pb \cdot Cl_6$
$H_8F_2Hg \cdot C_{12}$	$H_8Na \cdot C_{10}$
$H_8F_2HgO_4S_2 \cdot C_{12}$	$H_8O \cdot C_7$
$H_8F_2Zn \cdot C_{12}$	$H_8O \cdot C_{12}$
$H_8F_3LiOSe \cdot C_9$	$H_8O_2 \cdot C_4$
$H_8F_3LiSe \cdot C_{10}$	$H_8S \cdot C_7$
$H_8FeK_2 \cdot C_{10}$	$H_8S \cdot C_{12}$
$H_8FeNa_2 \cdot C_{10}$	$H_8Se \cdot C_7$
$H_8Ge \cdot C_2$	$H_9Al \cdot C_3$
$H_8Hg \cdot C_{12}$	$H_9BrCd \cdot C_4$
$H_8HgI_2 \cdot C_{12}$	$H_9BrClLiSn \cdot C_4$
$H_8HgN_2O_4 \cdot C_{12}$	$H_9BrGe \cdot C_3$
$H_8HgN_2O_8 \cdot C_{14}$	$H_9BrHg \cdot C_4$
$H_8HgN_6 \cdot C_5$	$H_9BrHg \cdot C_8$
$H_8HgO_2 \cdot C_5$	$H_9BrHgLiN \cdot C_8$
$H_8HgO_2 \cdot C_8$	$H_9BrHgO_2 \cdot C_5$
$H_8HgO_3 \cdot C_8$	$H_9BrHgO_2 \cdot C_8$
$H_8K \cdot C_{10}$	$H_9BrMg \cdot C_4$
$H_8K_2 \cdot C_6$	$H_9BrMgO \cdot C_9$
$H_8K_2 \cdot C_8$	$H_9BrMgO_2 \cdot C_8$
$H_8K_2 \cdot C_{10}$	$H_9BrPb \cdot C_3$
$H_8Li \cdot C_{10}$	$H_9BrSi \cdot C_3$
$H_8Li \cdot C_{12}$	$H_9BrSn \cdot C_3$
$H_8LiN \cdot C_3$	$H_9Br_2Li \cdot C_5$
$H_8LiN \cdot C_8$	$H_9Br_2LiSi \cdot C_4$
$H_8LiNO \cdot C_4$	$H_9Br_2LiSn \cdot C_4$
$H_8LiNO \cdot C_6$	$H_9CdCl \cdot C_4$
$H_8LiNOS \cdot C_3$	$H_9Cl \cdot C_8$
$H_8LiNOS \cdot C_8$	$H_9ClFLiS \cdot C_6$

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$H_9ClFeHg^*C_{10}$	$H_9Li^*C_{15}$
$H_9ClFeHgMnO_5^*C_{15}$	$H_9LiN_2^*C_6$
$H_9ClGe^*C_3$	$H_9LiN_2^*C_7$
$H_9ClHg^*C_4$	$H_9LiN_2Si^*C_4$
$H_9ClHg^*C_8$	$H_9LiN_4^*C_{12}$
$H_9ClHg^*C_{12}$	$H_9LiO^*C_4$
$H_9ClHgO^*C_6$	$H_9LiO^*C_5$
$H_9ClHgO^*C_8$	$H_9LiO^*C_6$
$H_9ClHgO^*C_9$	$H_9LiO^*C_8$
$H_9ClHgO_2^*C_8$	$H_9LiO^*C_{12}$
$H_9ClHgO_2^*C_9$	$H_9LiOS^*C_5$
$H_9ClMg^*C_4$	$H_9LiOS^*C_7$
$H_9ClPb^*C_3$	$H_9LiOS^*C_8$
$H_9ClSi^*C_3$	$H_9LiOS^*C_9$
$H_9ClSn^*C_3$	$H_9LiOS_2^*C_4$
$H_9Cl_2LiSi^*C_4$	$H_9LiOSe^*C_8$
$H_9Cl_2LiSn^*C_4$	$H_9LiO_2^*C_5$
$H_9Cl_3GeHgSi^*C_3$	$H_9LiO_2^*C_8$
$H_9Cl_3HgSi_2^*C_3$	$H_9LiO_2^*C_9$
$H_9Cl_3Si_2^*C_3$	$H_9LiO_2S^*C_6$
$H_9CrN_3O_3^*C_3$	$H_9LiO_2S^*C_9$
$H_9Cs^*C_4$	$H_9LiO_2S^*C_{12}$
$H_9Cs^*C_8$	$H_9LiO_2Se^*C_9$
$H_9CsO^*C_4$	$H_9LiO_3^*C_9$
$H_9Cu^*C_8$	$H_9LiO_3S^*C_5$
$H_9F_3LiS^*C_9$	$H_9LiO_3S^*C_8$
$H_9F_9Sn^*C_{10}$	$H_9LiO_4^*C_5$
$H_9FeLi^*C_{10}$	$H_9LiPb^*C_3$
$H_9GeLi^*C_3$	$H_9LiS^*C_6$
$H_9GeLi^*C_6$	$H_9LiS^*C_8$
$H_9HgI^*C_4$	$H_9LiS^*C_9$
$H_9HgI^*C_8$	$H_9LiS_2^*C_5$
$H_9Hg_3N^*C_5$	$H_9LiS_2^*C_6$
$H_9Hg_3NO_3^*C_8$	$H_9LiS_3^*C_5$
$H_9Hg_3O_4P^*C_3$	$H_9LiSe^*C_9$
$H_9K^*C_4$	$H_9LiSi^*C_3$
$H_9K^*C_9$	$H_9LiSn^*C_3$
$H_9K^*C_{11}$	$H_9Li_2N^*C_8$
$H_9K^*C_{13}$	$H_9Li_2NO^*C_4$
$H_9KO^*C_4$	$H_9Li_2NO^*C_9$
$H_9KO^*C_{13}$	$H_9Li_2NOS^*C_8$
$H_9KPb^*C_3$	$H_9Li_2NS^*C_9$
$H_9KSi^*C_3$	$H_9Li_3^*C_7$
$H_9KSn^*C_3$	$H_9Li_3^*C_9$
$H_9Li^*C_4$	$H_9Na^*C_4$
$H_9Li^*C_5$	$H_9Na^*C_7$
$H_9Li^*C_6$	$H_9Na^*C_8$
$H_9Li^*C_8$	$H_9Na^*C_{11}$
$H_9Li^*C_9$	$H_9NaO^*C_4$
$H_9Li^*C_{10}$	$H_9NaOSi^*C_3$
$H_9Li^*C_{12}$	$H_9NaO_2Si^*C_3$
$H_9Li^*C_{13}$	$H_9NaPb^*C_3$

$H_9NaPb^*C_6$	$H_{10}Hg^*C_{12}$
$H_9NaSi^*C_3$	$H_{10}Hg^*C_{16}$
$H_9NaSn^*C_3$	$H_{10}HgN_2^*C_{10}$
$H_9NaSn^*C_6$	$H_{10}HgN_2O_6S_2^*C_{22}$
$H_{10}AgN^*C_8$	$H_{10}HgN_4O_4^*C_8$
$H_{10}AlCl^*C_4$	$H_{10}HgO_2^*C_6$
$H_{10}AsLi^*C_{12}$	$H_{10}HgO_2^*C_{12}$
$H_{10}AuClZn^*C_{12}$	$H_{10}HgO_2S^*C_8$
$H_{10}Au_2Cl_4^*C_{12}$	$H_{10}HgO_2S^*C_{12}$
$H_{10}BClFeO_2^*C_{10}$	$H_{10}HgO_3^*C_9$
$H_{10}B_{20}Zn^*C_{16}$	$H_{10}HgO_4^*C_6$
$H_{10}BrCdF_2O_3P^*C_5$	$H_{10}HgO_4S_2^*C_{12}$
$H_{10}BrLi^*C_5$	$H_{10}HgS_2^*C_{16}$
$H_{10}BrLi^*C_{14}$	$H_{10}Hg_2O_4^*C_{10}$
$H_{10}Br_2Ge^*C_{12}$	$H_{10}K^*C_9$
$H_{10}Br_2Hg_2^*C_5$	$H_{10}K^*C_{12}$
$H_{10}Br_2Mg_2^*C_5$	$H_{10}K^*C_{14}$
$H_{10}Br_2SiZn_2^*C_4$	$H_{10}K_2^*C_9$
$H_{10}Br_2Zn_2^*C_6$	$H_{10}K_2^*C_{12}$
$H_{10}^*C_6$	$H_{10}K_2^*C_{14}$
$H_{10}^*C_9$	$H_{10}Li^*C_8$
$H_{10}Cd^*C_4$	$H_{10}Li^*C_9$
$H_{10}Cd^*C_{10}$	$H_{10}Li^*C_{12}$
$H_{10}Cd^*C_{12}$	$H_{10}Li^*C_{13}$
$H_{10}Cd^*C_{16}$	$H_{10}Li^*C_{14}$
$H_{10}CdN_4O_4^*C_8$	$H_{10}LiN^*C_8$
$H_{10}ClF_5Si^*C_{18}$	$H_{10}LiN^*C_9$
$H_{10}ClHgNO_2^*C_6$	$H_{10}LiN^*C_{10}$
$H_{10}ClHgN_3^*C_6$	$H_{10}LiN^*C_{11}$
$H_{10}ClLi^*C_{11}$	$H_{10}LiN^*C_{12}$
$H_{10}ClLiSi^*C_4$	$H_{10}LiNO^*C_5$
$H_{10}Cl_2Hg^*C_{13}$	$H_{10}LiNO^*C_{15}$
$H_{10}Cl_2LiO_3P^*C_5$	$H_{10}LiNOS^*C_8$
$H_{10}Cl_2Pb^*C_{12}$	$H_{10}LiNO_2S^*C_5$
$H_{10}Cl_2Sn^*C_4$	$H_{10}LiNO_2S^*C_8$
$H_{10}Cl_2Sn^*C_{12}$	$H_{10}LiNO_3^*C_5$
$H_{10}Cl_4Hg_3O_4^*C_8$	$H_{10}LiNO_3S^*C_9$
$H_{10}Cr_2HgO_6^*C_{18}$	$H_{10}LiNS_2^*C_6$
$H_{10}Cs_2^*C_{12}$	$H_{10}LiNS_2^*C_9$
$H_{10}CuN^*C_8$	$H_{10}LiNS_3^*C_5$
$H_{10}F_4HgO^*C_{14}$	$H_{10}LiNSi^*C_5$
$H_{10}F_4HgO_3^*C_{15}$	$H_{10}LiN_4^*C_{12}$
$H_{10}F_{10}HgN_2O_6S_2^*C_{22}$	$H_{10}LiP^*C_{12}$
$H_{10}Fe^*C_{10}$	$H_{10}LiPS^*C_8$
$H_{10}FeLiN^*C_{12}$	$H_{10}LiSb^*C_{12}$
$H_{10}FeMnO_5^*C_{15}$	$H_{10}Li_2^*C_5$
$H_{10}GeLi_2^*C_{12}$	$H_{10}Li_2^*C_7$
$H_{10}GeNa_2^*C_{12}$	$H_{10}Li_2^*C_{10}$
$H_{10}Hg^*C_4$	$H_{10}Li_2^*C_{12}$
$H_{10}Hg^*C_6$	$H_{10}Li_2^*C_{14}$
$H_{10}Hg^*C_8$	$H_{10}Li_2^*C_{16}$
$H_{10}Hg^*C_{10}$	$H_{10}Li_2O^*C_5$



- $H_{10}Li_2O^*C_9$   
 $H_{10}Li_2O^*C_{13}$   
 $H_{10}Li_2O_2^*C_6$   
 $H_{10}Li_2O_2^*C_{15}$   
 $H_{10}Li_2O_2Si^*C_5$   
 $H_{10}Li_2O_4^*C_{14}$   
 $H_{10}Li_2Pb^*C_{12}$   
 $H_{10}Li_2Sn^*C_{12}$   
 $H_{10}Li_4^*C_{16}$   
 $H_{10}N_4O_4Zn^*C_8$   
 $H_{10}Na^*C_{12}$   
 $H_{10}Na^*C_{14}$   
 $H_{10}Na_2^*C_{14}$   
 $H_{10}Na_2Sn^*C_4$   
 $H_{10}Na_2Sn^*C_{12}$   
 $H_{10}O^*C_6$   
 $H_{10}O^*C_{13}$   
 $H_{10}OZn^*C_5$   
 $H_{10}O_4S^*C_4$   
 $H_{10}O_4SZn^*C_4$   
 $H_{10}O_4Zn^*C_{14}$   
 $H_{10}Pb^*C_{12}$   
 $H_{10}Rb^*C_{12}$   
 $H_{10}Sn^*C_3$   
 $H_{10}Sn^*C_{12}$   
 $H_{10}V^*C_{10}$   
 $H_{10}Zn^*C_4$   
 $H_{10}Zn^*C_6$   
 $H_{10}Zn^*C_{10}$   
 $H_{10}Zn^*C_{12}$   
 $H_{10}Zn^*C_{14}$   
 $H_{10}Zn^*C_{16}$   
 $H_{11}BFeO_2^*C_{10}$   
 $H_{11}BO_2^*C_8$   
 $H_{11}BrFeHgO^*C_{12}$   
 $H_{11}BrHg^*C_{14}$   
 $H_{11}BrHgLiN^*C_9$   
 $H_{11}BrHg_2O_2S^*C_{10}$   
 $H_{11}BrLiN^*C_6$   
 $H_{11}BrMg^*C_5$   
 $H_{11}BrMg^*C_6$   
 $H_{11}BrZn^*C_6$   
 $H_{11}Cl^*C_5$   
 $H_{11}Cl^*C_9$   
 $H_{11}ClFLiSi^*C_9$   
 $H_{11}ClFeHg^*C_{12}$   
 $H_{11}ClGe^*C_8$   
 $H_{11}ClHg^*C_6$   
 $H_{11}ClHgO^*C_6$   
 $H_{11}ClHgO_2^*C_9$   
 $H_{11}ClHgO_2S^*C_6$   
 $H_{11}ClHgSi^*C_4$   
 $H_{11}ClLiN^*C_9$   
 $H_{11}ClLiO_2PS^*C_5$   
 $H_{11}ClLiO_3P^*C_5$   
 $H_{11}ClMgO^*C_5$   
 $H_{11}ClMgS^*C_5$   
 $H_{11}ClMgSi^*C_4$   
 $H_{11}ClSi^*C_4$   
 $H_{11}ClSi^*C_8$   
 $H_{11}ClSi^*C_{12}$   
 $H_{11}ClSn^*C_5$   
 $H_{11}Cl_2FHg_2O^*C_{15}$   
 $H_{11}Cl_2Hg_2O^*C_{12}$   
 $H_{11}Cl_2LiSi^*C_6$   
 $H_{11}Cl_3GeHgSi^*C_4$   
 $H_{11}Cs^*C_{13}$   
 $H_{11}CsSi^*C_4$   
 $H_{11}D_2ClHg^*C_6$   
 $H_{11}FeLi^*C_{11}$   
 $H_{11}GeLi^*C_8$   
 $H_{11}GeLi^*C_{12}$   
 $H_{11}HgIO^*C_9$   
 $H_{11}HgN^*C_{15}$   
 $H_{11}HgNO_2^*C_9$   
 $H_{11}HgNO_3^*C_{10}$   
 $H_{11}Hg_2NO_4^*C_{10}$   
 $H_{11}Hg_2O_4^*C_9$   
 $H_{11}K^*C_5$   
 $H_{11}K^*C_9$   
 $H_{11}K^*C_{13}$   
 $H_{11}KO_2^*C_{15}$   
 $H_{11}KSi^*C_4$   
 $H_{11}Li^*C_5$   
 $H_{11}Li^*C_6$   
 $H_{11}Li^*C_7$   
 $H_{11}Li^*C_8$   
 $H_{11}Li^*C_9$   
 $H_{11}Li^*C_{10}$   
 $H_{11}Li^*C_{13}$   
 $H_{11}Li^*C_{14}$   
 $H_{11}LiMnNO_3^*C_{11}$   
 $H_{11}LiNO_3P^*C_6$   
 $H_{11}LiN_2^*C_5$   
 $H_{11}LiN_2^*C_6$   
 $H_{11}LiN_2^*C_7$   
 $H_{11}LiN_2^*C_{11}$   
 $H_{11}LiO^*C_5$   
 $H_{11}LiO^*C_{11}$   
 $H_{11}LiOS^*C_5$   
 $H_{11}LiOS^*C_{10}$   
 $H_{11}LiOS_2^*C_6$   
 $H_{11}LiOSe^*C_9$   
 $H_{11}LiOSe^*C_{11}$

$H_{11}LiOSe^*C_{13}$	$H_{12}^*C_8$
$H_{11}LiOSe^*C_{14}$	$H_{12}ClFHgO^*C_{15}$
$H_{11}LiOSi^*C_4$	$H_{12}ClHgN^*C_9$
$H_{11}LiOSi^*C_5$	$H_{12}ClLiSi^*C_6$
$H_{11}LiO_2^*C_5$	$H_{12}ClLi_2NO^*C_{10}$
$H_{11}LiO_2^*C_6$	$H_{12}Cl_2Hg^*C_{14}$
$H_{11}LiO_2^*C_7$	$H_{12}Cl_2HgSi_2^*C_4$
$H_{11}LiO_2^*C_8$	$H_{12}Cl_2Hg_2O_2^*C_6$
$H_{11}LiO_2^*C_9$	$H_{12}Cl_2Si_2^*C_4$
$H_{11}LiO_2^*C_{11}$	$H_{12}Cl_3Sb^*C_{18}$
$H_{11}LiO_2S^*C_6$	$H_{12}Cl_8HgN_2O_6S_2^*C_{22}$
$H_{11}LiO_2S^*C_{10}$	$H_{12}CsN^*C_6$
$H_{11}LiO_2Se^*C_{11}$	$H_{12}Cs_2^*C_{12}$
$H_{11}LiO_4^*C_8$	$H_{12}F_2Sn^*C_6$
$H_{11}LiS^*C_9$	$H_{12}F_8HgN_2O_6S_2^*C_{22}$
$H_{11}LiS^*C_{10}$	$H_{12}F_{10}HgSi_2^*C_{16}$
$H_{11}LiS^*C_{11}$	$H_{12}Ge^*C_{12}$
$H_{11}LiS^*C_{13}$	$H_{12}GeO^*C_4$
$H_{11}LiS^*C_{14}$	$H_{12}Ge_2Hg^*C_3$
$H_{11}LiS_2^*C_6$	$H_{12}HgN_2^*C_8$
$H_{11}LiS_2^*C_{13}$	$H_{12}HgN_2^*C_{16}$
$H_{11}LiSe^*C_{10}$	$H_{12}HgO_2^*C_7$
$H_{11}LiSe^*C_{13}$	$H_{12}HgO_2^*C_{10}$
$H_{11}LiSe^*C_{14}$	$H_{12}HgO_2S^*C_{13}$
$H_{11}LiSe_2^*C_{13}$	$H_{12}HgO_2Si^*C_7$
$H_{11}LiSi^*C_4$	$H_{12}HgO_3^*C_7$
$H_{11}LiSi^*C_5$	$H_{12}HgO_4^*C_7$
$H_{11}LiSi^*C_6$	$H_{12}HgO_4^*C_8$
$H_{11}LiSi^*C_8$	$H_{12}HgSi^*C_6$
$H_{11}LiSi^*C_{12}$	$H_{12}HgSi_2^*C_3$
$H_{11}LiTe_2^*C_{13}$	$H_{12}Li^*C_{14}$
$H_{11}Li_2N^*C_9$	$H_{12}Li^*C_{20}$
$H_{11}Li_2NO^*C_{14}$	$H_{12}LiN^*C_6$
$H_{11}N^*C_9$	$H_{12}LiN^*C_7$
$H_{11}Na^*C_5$	$H_{12}LiN^*C_9$
$H_{11}Na^*C_{13}$	$H_{12}LiN^*C_{10}$
$H_{11}NaSi^*C_4$	$H_{12}LiN^*C_{14}$
$H_{11}NaSn^*C_{12}$	$H_{12}LiN^*C_{16}$
$H_{11}P^*C_4$	$H_{12}LiNO^*C_{11}$
$H_{11}Rb^*C_{13}$	$H_{12}LiNOS^*C_7$
$H_{11}RbSi^*C_4$	$H_{12}LiNOS_2^*C_7$
$H_{12}AgN^*C_9$	$H_{12}LiNO_2^*C_6$
$H_{12}Ag_2BrN^*C_9$	$H_{12}LiNO_2^*C_9$
$H_{12}AsClMg^*C_5$	$H_{12}LiNO_3S_2^*C_9$
$H_{12}AsLi^*C_{13}$	$H_{12}LiN_3^*C_{15}$
$H_{12}AsLiO^*C_{13}$	$H_{12}LiOP^*C_{13}$
$H_{12}Au_3N_3^*C_{15}$	$H_{12}LiO_4P^*C_6$
$H_{12}BiCl_3^*C_{18}$	$H_{12}LiP^*C_{13}$
$H_{12}BrLiO_2^*C_{10}$	$H_{12}LiSb^*C_{13}$
$H_{12}BrNOZn^*C_6$	$H_{12}Li_2^*C_6$
$H_{12}Br_2Hg_2O^*C_6$	$H_{12}Li_2^*C_{10}$
$H_{12}Br_3Sb^*C_{18}$	$H_{12}Li_2^*C_{14}$

$H_{12}Li_2 * C_{16}$	$H_{13}K * C_{19}$
$H_{12}Li_2 * C_{18}$	$H_{13}Li * C_6$
$H_{12}Li_2 * C_{20}$	$H_{13}Li * C_7$
$H_{12}Li_2O * C_6$	$H_{13}Li * C_8$
$H_{12}Li_2O * C_{10}$	$H_{13}Li * C_9$
$H_{12}Li_2O * C_{12}$	$H_{13}Li * C_{10}$
$H_{12}Li_2O_2 * C_8$	$H_{13}Li * C_{11}$
$H_{12}Li_2O_2 * C_{16}$	$H_{13}Li * C_{14}$
$H_{12}Li_2O_4 * C_{10}$	$H_{13}Li * C_{15}$
$H_{12}Li_2Zn * C_4$	$H_{13}Li * C_{19}$
$H_{12}Li_4 * C_{14}$	$H_{13}LiN_2 * C_6$
$H_{12}OS * C_{10}$	$H_{13}LiO * C_7$
$H_{12}OSi * C_4$	$H_{13}LiO * C_8$
$H_{12}OSn * C_4$	$H_{13}LiO * C_{10}$
$H_{12}OZn * C_{10}$	$H_{13}LiOS_2 * C_{12}$
$H_{12}Pb * C_4$	$H_{13}LiOSE * C_{14}$
$H_{12}Pb * C_8$	$H_{13}LiOSi * C_5$
$H_{12}S_2 * C_{13}$	$H_{13}LiOSi * C_6$
$H_{12}S_4 * C_6$	$H_{13}LiO_2 * C_6$
$H_{12}Se * C_5$	$H_{13}LiO_2 * C_8$
$H_{12}Se_2 * C_{13}$	$H_{13}LiO_2 * C_{11}$
$H_{12}Si * C_4$	$H_{13}LiO_2S * C_{11}$
$H_{12}Si * C_5$	$H_{13}LiO_2Se * C_9$
$H_{12}Si * C_{12}$	$H_{13}LiO_3 * C_9$
$H_{12}Sn * C_4$	$H_{13}LiO_3S * C_{15}$
$H_{12}Sn * C_6$	$H_{13}LiP_2 * C_5$
$H_{12}Sn * C_7$	$H_{13}LiS * C_8$
$H_{12}Sn * C_8$	$H_{13}LiS * C_{10}$
$H_{12}Sn * C_{12}$	$H_{13}LiS * C_{11}$
$H_{12}Te_2 * C_{13}$	$H_{13}LiS * C_{14}$
$H_{12}Zn * C_{10}$	$H_{13}LiS_2 * C_9$
$H_{13}AuBr_3N * C_9$	$H_{13}LiS_2 * C_{14}$
$H_{13}BO_2 * C_9$	$H_{13}LiSe * C_{14}$
$H_{13}B_2LiO_4 * C_7$	$H_{13}LiSe_2 * C_{14}$
$H_{13}BrHg * C_7$	$H_{13}LiSi * C_5$
$H_{13}BrHgLiN * C_{14}$	$H_{13}LiSi * C_6$
$H_{13}ClHg * C_6$	$H_{13}LiSi * C_{13}$
$H_{13}ClHg * C_9$	$H_{13}LiSn * C_{13}$
$H_{13}ClHgO * C_7$	$H_{13}Li_2N * C_7$
$H_{13}ClHgO_2 * C_8$	$H_{13}Li_2N * C_{11}$
$H_{13}ClHgO_2S * C_6$	$H_{13}Li_2N * C_{14}$
$H_{13}ClHgO_2S * C_{12}$	$H_{13}Li_2NO * C_8$
$H_{13}ClHgO_3 * C_8$	$H_{13}Li_2NO * C_{10}$
$H_{13}ClLiN_2OP * C_5$	$H_{13}Li_2NO * C_{11}$
$H_{13}ClMg * C_7$	$H_{13}Li_2NO_2 * C_{11}$
$H_{13}ClSi * C_{13}$	$H_{13}Li_2N_2O_2S * C_{11}$
$H_{13}ClSnZn * C_{13}$	$H_{13}Na * C_7$
$H_{13}CuN_2 * C_{18}$	$H_{13}Na * C_{14}$
$H_{13}FeLi_2N * C_{12}$	$H_{13}NaO * C_6$
$H_{13}K * C_{10}$	$H_{13}NaSi * C_{13}$
$H_{13}K * C_{14}$	$H_{14}AsLi * C_{10}$
$H_{13}K * C_{15}$	$H_{14}AsLiO * C_{14}$

$H_{14}^*C_{16}$	$H_{14}LiNO_3S_2^*C_{14}$
$H_{14}Cd^*C_6$	$H_{14}LiNS^*C_6$
$H_{14}Cd^*C_8$	$H_{14}LiNS^*C_7$
$H_{14}Cd^*C_{14}$	$H_{14}LiNS^*C_{11}$
$H_{14}ClHgN^*C_6$	$H_{14}LiN_2OP^*C_5$
$H_{14}ClHgNO^*C_8$	$H_{14}LiOP^*C_{12}$
$H_{14}Cl_2HgSn^*C_6$	$H_{14}LiOP^*C_{14}$
$H_{14}Cl_2Hg_2^*C_{16}$	$H_{14}LiOPS^*C_8$
$H_{14}Cl_2Si_2^*C_5$	$H_{14}LiO_2P^*C_8$
$H_{14}CsN^*C_6$	$H_{14}LiO_3PS^*C_6$
$H_{14}CuO_2^*C_{10}$	$H_{14}LiO_4P^*C_7$
$H_{14}F_3LiSeSi^*C_{11}$	$H_{14}LiO_5P^*C_7$
$H_{14}FeLiN^*C_{12}$	$H_{14}LiO_5PS^*C_6$
$H_{14}FeO^*C_{12}$	$H_{14}LiPS^*C_{12}$
$H_{14}FeO_2^*C_{15}$	$H_{14}Li_2^*C_{15}$
$H_{14}GeLi_2^*C_{14}$	$H_{14}Li_2^*C_{16}$
$H_{14}Ge_2^*C_{12}$	$H_{14}Li_2^*C_{18}$
$H_{14}Hg^*C_6$	$H_{14}Li_2^*C_{22}$
$H_{14}Hg^*C_8$	$H_{14}Li_2O^*C_7$
$H_{14}Hg^*C_{12}$	$H_{14}Li_2O^*C_{11}$
$H_{14}Hg^*C_{14}$	$H_{14}Li_2O^*C_{15}$
$H_{14}Hg^*C_{20}$	$H_{14}Li_2O^*C_{20}$
$H_{14}HgN_2O_4^*C_8$	$H_{14}Li_2O_2S^*C_{17}$
$H_{14}HgO_2^*C_8$	$H_{14}NNa^*C_6$
$H_{14}HgO_2^*C_{11}$	$H_{14}Na_2Sn^*C_6$
$H_{14}HgO_2^*C_{14}$	$H_{14}O^*C_{10}$
$H_{14}HgO_2^*C_{16}$	$H_{14}O^*C_{11}$
$H_{14}HgO_2^*C_{18}$	$H_{14}OS^*C_{10}$
$H_{14}HgO_3^*C_8$	$H_{14}OS^*C_{11}$
$H_{14}HgO_4^*C_{10}$	$H_{14}OSe_2^*C_{14}$
$H_{14}HgO_4^*C_{16}$	$H_{14}O_3^*C_8$
$H_{14}HgO_4S_2^*C_{14}$	$H_{14}O_4Zn^*C_{16}$
$H_{14}HgO_6S_2^*C_{15}$	$H_{14}S^*C_{10}$
$H_{14}HgO_8^*C_{10}$	$H_{14}S^*C_{14}$
$H_{14}HgS_2^*C_{14}$	$H_{14}S_2^*C_{14}$
$H_{14}HgSi_2^*C_4$	$H_{14}S_2^*C_{15}$
$H_{14}KN^*C_6$	$H_{14}S_2Zn^*C_{14}$
$H_{14}K_2^*C_{18}$	$H_{14}Se_2^*C_{15}$
$H_{14}K_4^*C_{18}$	$H_{14}Si^*C_9$
$H_{14}LiN^*C_8$	$H_{14}Sn^*C_6$
$H_{14}LiN^*C_{10}$	$H_{14}Sn^*C_{13}$
$H_{14}LiN^*C_{12}$	$H_{14}Zn^*C_6$
$H_{14}LiNO^*C_7$	$H_{14}Zn^*C_8$
$H_{14}LiNO^*C_9$	$H_{14}Zn^*C_{10}$
$H_{14}LiNO^*C_{10}$	$H_{14}Zn^*C_{14}$
$H_{14}LiNO^*C_{11}$	$H_{14}Zn^*C_{20}$
$H_{14}LiNOSi^*C_7$	$H_{15}Al^*C_6$
$H_{14}LiNOSi^*C_8$	$H_{15}As^*C_{18}$
$H_{14}LiNOSi^*C_{11}$	$H_{15}AsHg_3O_4^*C_6$
$H_{14}LiNO_2^*C_9$	$H_{15}AuClF_{10}P^*C_{30}$
$H_{14}LiNO_2^*C_{12}$	$H_{15}AuClP^*C_{18}$
$H_{14}LiNO_2S^*C_{12}$	$H_{15}AuCl_2F_5^*C_{24}$

- $H_{15}AuCl_3PSn^*C_{18}$   
 $H_{15}AuF_5O_2P^*C_{25}$   
 $H_{15}AuF_5P^*C_{24}$   
 $H_{15}Bj^*C_6$   
 $H_{15}BrCuP^*C_{18}$   
 $H_{15}BrGe^*C_6$   
 $H_{15}BrGe^*C_{18}$   
 $H_{15}BrHg^*C_{16}$   
 $H_{15}BrHgO_2^*C_7$   
 $H_{15}BrSn^*C_6$   
 $H_{15}BrSn^*C_{18}$   
 $H_{15}Br_2Hg_2N^*C_{12}$   
 $H_{15}CdClSn^*C_{18}$   
 $H_{15}CdLi^*C_{18}$   
 $H_{15}Cl^*C_{19}$   
 $H_{15}ClGe^*C_6$   
 $H_{15}ClGe^*C_{18}$   
 $H_{15}ClHg^*C_8$   
 $H_{15}ClHgO^*C_{16}$   
 $H_{15}ClHgO_2^*C_{16}$   
 $H_{15}ClHgPb^*C_{18}$   
 $H_{15}ClHgSn^*C_{18}$   
 $H_{15}ClPb^*C_{18}$   
 $H_{15}ClSi^*C_{18}$   
 $H_{15}ClSn^*C_6$   
 $H_{15}ClSn^*C_{18}$   
 $H_{15}ClSnZn^*C_{18}$   
 $H_{15}Cl_2LiPb^*C_{19}$   
 $H_{15}CrLiO_4S^*C_{21}$   
 $H_{15}Cs^*C_{13}$   
 $H_{15}Cs^*C_{19}$   
 $H_{15}CsGe^*C_6$   
 $H_{15}CsSi^*C_6$   
 $H_{15}CsSi^*C_{18}$   
 $H_{15}FGe^*C_{18}$   
 $H_{15}FSi^*C_{18}$   
 $H_{15}F_3HgO_3^*C_9$   
 $H_{15}F_{15}Ge_2^*C_{24}$   
 $H_{15}F_{15}Ge_2Hg^*C_{24}$   
 $H_{15}GeK^*C_6$   
 $H_{15}GeK^*C_{18}$   
 $H_{15}GeLi^*C_6$   
 $H_{15}GeLi^*C_{18}$   
 $H_{15}GeLiOS^*C_7$   
 $H_{15}GeNa^*C_6$   
 $H_{15}GeNa^*C_{18}$   
 $H_{15}Hg_3O_4P^*C_6$   
 $H_{15}K^*C_{11}$   
 $H_{15}K^*C_{13}$   
 $H_{15}K^*C_{19}$   
 $H_{15}KPb^*C_{18}$   
 $H_{15}KSi^*C_6$   
 $H_{15}KSi^*C_{18}$   
 $H_{15}K_2^*C_{15}$   
 $H_{15}K_2^*C_{19}$   
 $H_{15}Li^*C_7$   
 $H_{15}Li^*C_8$   
 $H_{15}Li^*C_{10}$   
 $H_{15}Li^*C_{15}$   
 $H_{15}Li^*C_{16}$   
 $H_{15}Li^*C_{17}$   
 $H_{15}Li^*C_{19}$   
 $H_{15}LiMoO_4S^*C_{21}$   
 $H_{15}LiNO_3P^*C_8$   
 $H_{15}LiN_2^*C_{11}$   
 $H_{15}LiN_2^*C_{15}$   
 $H_{15}LiO^*C_9$   
 $H_{15}LiO^*C_{19}$   
 $H_{15}LiOS^*C_7$   
 $H_{15}LiOSi^*C_7$   
 $H_{15}LiOSi^*C_{10}$   
 $H_{15}LiOS_2^*C_8$   
 $H_{15}LiOS_2^*C_9$   
 $H_{15}LiOS_2^*C_{13}$   
 $H_{15}LiOSe^*C_{15}$   
 $H_{15}LiOSi^*C_7$   
 $H_{15}LiO_2^*C_7$   
 $H_{15}LiO_2^*C_{11}$   
 $H_{15}LiO_2^*C_{12}$   
 $H_{15}LiO_2Si^*C_7$   
 $H_{15}LiO_3^*C_9$   
 $H_{15}LiO_4^*C_{10}$   
 $H_{15}LiO_4SW^*C_{21}$   
 $H_{15}LiPb^*C_6$   
 $H_{15}LiPb^*C_{18}$   
 $H_{15}LiS^*C_{11}$   
 $H_{15}LiS^*C_{13}$   
 $H_{15}LiS^*C_{20}$   
 $H_{15}LiSSi^*C_{10}$   
 $H_{15}LiS_2^*C_9$   
 $H_{15}LiS_2Si^*C_7$   
 $H_{15}LiS_2Sn^*C_6$   
 $H_{15}LiS_3^*C_{19}$   
 $H_{15}LiSe^*C_{11}$   
 $H_{15}LiSeSi^*C_{10}$   
 $H_{15}LiSe_3^*C_{19}$   
 $H_{15}LiSi^*C_6$   
 $H_{15}LiSi^*C_8$   
 $H_{15}LiSi^*C_{10}$   
 $H_{15}LiSi^*C_{18}$   
 $H_{15}LiSn^*C_6$   
 $H_{15}LiSn^*C_8$   
 $H_{15}LiSn^*C_{18}$

$H_{15}LiSn_2 * C_5$	$H_{16}LiP * C_{19}$
$H_{15}LiZn * C_{18}$	$H_{16}Li_2 * C_{16}$
$H_{15}Li_2N * C_{19}$	$H_{16}Li_2 * C_{18}$
$H_{15}Li_2NO * C_{12}$	$H_{16}Li_2O * C_8$
$H_{15}Li_2O_5P * C_{16}$	$H_{16}Li_2O * C_9$
$H_{15}N * C_{18}$	$H_{16}Li_2O * C_{13}$
$H_{15}N * C_{19}$	$H_{16}Li_2O * C_{20}$
$H_{15}NSi * C_7$	$H_{16}Li_2O_2S * C_8$
$H_{15}Na * C_{19}$	$H_{16}O * C_{13}$
$H_{15}Na * C_{21}$	$H_{16}OPbS * C_7$
$H_{15}NaPb * C_6$	$H_{16}OS * C_{11}$
$H_{15}NaPb * C_{10}$	$H_{16}OSSi * C_7$
$H_{15}NaPb * C_{18}$	$H_{16}OSSn * C_7$
$H_{15}NaSi * C_6$	$H_{16}S * C_{11}$
$H_{15}NaSi * C_{18}$	$H_{16}S * C_{12}$
$H_{15}NaSn * C_6$	$H_{16}S * C_{15}$
$H_{15}NaSn * C_{14}$	$H_{16}S * C_{19}$
$H_{15}NaSn * C_{18}$	$H_{16}SSi * C_{10}$
$H_{15}P * C_{18}$	$H_{16}SSn * C_{11}$
$H_{15}PbRb * C_{18}$	$H_{16}S_2 * C_{15}$
$H_{15}Rb * C_{19}$	$H_{16}S_2 * C_{16}$
$H_{15}RbSi * C_{18}$	$H_{16}S_2 * C_{19}$
$H_{15}Sb * C_{18}$	$H_{16}SeSi * C_6$
$H_{16}BrHgP * C_{19}$	$H_{16}SeSi * C_7$
$H_{16}Br_2CuHgP * C_{19}$	$H_{16}Se_2 * C_{16}$
$H_{16}ClFeHgN * C_{13}$	$H_{16}Se_2 * C_{20}$
$H_{16}ClHgN * C_8$	$H_{16}Se_3 * C_{19}$
$H_{16}ClHgNO * C_9$	$H_{16}Si * C_6$
$H_{16}Cl_2Hg_2O_2 * C_{16}$	$H_{16}Si * C_{15}$
$H_{16}Cu_4F_{12} * C_{28}$	$H_{16}Si * C_{17}$
$H_{16}FeLiN * C_{13}$	$H_{16}Si * C_{18}$
$H_{16}Ge * C_6$	$H_{16}Sn * C_6$
$H_{16}Ge * C_{17}$	$H_{16}Sn * C_7$
$H_{16}Ge * C_{18}$	$H_{16}Sn * C_{18}$
$H_{16}GeOS * C_7$	$H_{16}Zn * C_8$
$H_{16}HgO_2 * C_9$	$H_{16}Zn_2 * C_8$
$H_{16}HgO_4 * C_{17}$	$H_{17}BrHgN_2 * C_{15}$
$H_{16}HgSi_2 * C_6$	$H_{17}BrMg * C_8$
$H_{16}Hg_2 * C_8$	$H_{17}Cl * C_{20}$
$H_{16}Hg_2O_8S_2 * C_{17}$	$H_{17}ClHgO * C_9$
$H_{16}LiN * C_{13}$	$H_{17}ClHgSi * C_8$
$H_{16}LiNO * C_{13}$	$H_{17}GeLi * C_7$
$H_{16}LiNOSi * C_7$	$H_{17}GeLi * C_{19}$
$H_{16}LiNO_2 * C_{12}$	$H_{17}K * C_8$
$H_{16}LiNP_2 * C_6$	$H_{17}Li * C_8$
$H_{16}LiNSSi * C_7$	$H_{17}Li * C_9$
$H_{16}LiN_2OP * C_7$	$H_{17}Li * C_{10}$
$H_{16}LiN_2O_2P * C_7$	$H_{17}Li * C_{16}$
$H_{16}LiOP * C_{15}$	$H_{17}Li * C_{17}$
$H_{16}LiOP * C_{16}$	$H_{17}Li * C_{21}$
$H_{16}LiOPS * C_{19}$	$H_{17}LiN * C_{23}$
$H_{16}LiO_3P * C_8$	$H_{17}LiN_3OP * C_6$

$H_{17}LiO^*C_8$	$H_{18}Hg^*C_{24}$
$H_{17}LiO^*C_9$	$H_{18}HgN_4^*C_{14}$
$H_{17}LiOS^*C_9$	$H_{18}HgN_4O_2^*C_{12}$
$H_{17}LiOS^*C_{21}$	$H_{18}HgO_2^*C_{10}$
$H_{17}LiOSe^*C_{14}$	$H_{18}HgO_2^*C_{12}$
$H_{17}LiOSi^*C_7$	$H_{18}HgO_2^*C_{18}$
$H_{17}LiOSi^*C_{20}$	$H_{18}HgO_3^*C_9$
$H_{17}LiO_2^*C_9$	$H_{18}HgO_6^*C_{12}$
$H_{17}LiO_2^*C_{12}$	$H_{18}HgSiSn^*C_6$
$H_{17}LiO_2S^*C_{21}$	$H_{18}HgSi_2^*C_6$
$H_{17}LiO_3^*C_{12}$	$H_{18}HgSn^*C_7$
$H_{17}LiPb^*C_{19}$	$H_{18}HgSn_2^*C_6$
$H_{17}LiS^*C_{12}$	$H_{18}LiN^*C_{10}$
$H_{17}LiS^*C_{14}$	$H_{18}LiN^*C_{17}$
$H_{17}LiS^*C_{21}$	$H_{18}LiN^*C_{20}$
$H_{17}LiS_2^*C_9$	$H_{18}LiNO_2S^*C_{16}$
$H_{17}LiSe^*C_{12}$	$H_{18}LiNSe^*C_{14}$
$H_{17}LiSi^*C_{17}$	$H_{18}LiO_5P^*C_8$
$H_{17}LiSn^*C_{11}$	$H_{18}LiP^*C_8$
$H_{17}LiSn^*C_{19}$	$H_{18}LiPS^*C_{13}$
$H_{17}LiSn^*C_{20}$	$H_{18}LiP_3^*C_7$
$H_{17}Li_2N^*C_{23}$	$H_{18}Li_2^*C_{18}$
$H_{17}Li_3^*C_{21}$	$H_{18}Li_2^*C_{26}$
$H_{17}NSi^*C_{18}$	$H_{18}Li_2O^*C_9$
$H_{17}Na^*C_{20}$	$H_{18}Li_2O^*C_{13}$
$H_{18}AsLi^*C_{16}$	$H_{18}Li_2Si^*C_{18}$
$H_{18}AuP^*C_6$	$H_{18}Li_4^*C_{28}$
$H_{18}AuP^*C_{19}$	$H_{18}NNaSi_2^*C_6$
$H_{18}BLiP_2^*C_6$	$H_{18}Na_2Sn^*C_8$
$H_{18}B_3LiO_6^*C_{10}$	$H_{18}O^*C_{14}$
$H_{18}BrClSn_2^*C_7$	$H_{18}OS^*C_{16}$
$H_{18}BrLiSi_2^*C_7$	$H_{18}O_2Pb^*C_{20}$
$H_{18}Br_2Sn_2^*C_7$	$H_{18}O_2Si_2^*C_6$
$H_{18}CdO_6^*C_{12}$	$H_{18}O_4Si_2^*C_6$
$H_{18}ClLiO_2Si^*C_9$	$H_{18}Pb^*C_{20}$
$H_{18}ClLiSi^*C_8$	$H_{18}Pb_2^*C_6$
$H_{18}Cl_2Ge^*C_8$	$H_{18}S^*C_{12}$
$H_{18}Cl_2Hg_2O_2^*C_{11}$	$H_{18}S^*C_{16}$
$H_{18}Cl_2Pb^*C_{21}$	$H_{18}S^*C_{20}$
$H_{18}Cl_2Sn_2^*C_7$	$H_{18}SSi^*C_{11}$
$H_{18}FeLiN^*C_{14}$	$H_{18}SSi^*C_{12}$
$H_{18}Ge^*C_7$	$H_{18}S_2^*C_{16}$
$H_{18}Ge^*C_{18}$	$H_{18}S_2^*C_{17}$
$H_{18}Ge^*C_{20}$	$H_{18}Se_3^*C_{20}$
$H_{18}GeHgSi^*C_6$	$H_{18}Si^*C_{18}$
$H_{18}GeK_2^*C_8$	$H_{18}Si^*C_{20}$
$H_{18}Ge_2^*C_{12}$	$H_{18}Si_2^*C_6$
$H_{18}Ge_2Hg^*C_6$	$H_{18}Si_2^*C_7$
$H_{18}Hg^*C_8$	$H_{18}Sn^*C_8$
$H_{18}Hg^*C_{10}$	$H_{18}Sn^*C_{10}$
$H_{18}Hg^*C_{12}$	$H_{18}Sn^*C_{12}$
$H_{18}Hg^*C_{16}$	$H_{18}Sn^*C_{20}$

$H_{18}Sn_2^*C_6$	$H_{20}AlNa^*C_8$
$H_{18}Sn_2^*C_{12}$	$H_{20}AuO^*C_{21}$
$H_{18}Zn^*C_8$	$H_{20}AuP^*C_{18}$
$H_{18}Zn^*C_{10}$	$H_{20}AuP^*C_{20}$
$H_{18}Zn^*C_{16}$	$H_{20}AuP^*C_{23}$
$H_{18}Zn^*C_{26}$	$H_{20}AuP^*C_{24}$
$H_{19}AuCl_2S^*C_{12}$	$H_{20}BaZn^*C_8$
$H_{19}AuO^*C_7$	$H_{20}BrSb^*C_{24}$
$H_{19}BrGe^*C_{12}$	$H_{20}Br_2Ge_2^*C_{24}$
$H_{19}BrHgSi_2^*C_7$	$H_{20}CaZn^*C_8$
$H_{19}ClHgO_2^*C_{11}$	$H_{20}CdF_4O_2P_2^*C_{10}$
$H_{19}ClPb^*C_{21}$	$H_{20}ClHg^*C_{10}$
$H_{19}ClSi^*C_{12}$	$H_{20}ClLiO_6P_2^*C_9$
$H_{19}ClSi^*C_{16}$	$H_{20}Cl_2Hg^*C_{26}$
$H_{19}ClSi^*C_{20}$	$H_{20}Cl_2HgPb^*C_{25}$
$H_{19}Cs^*C_{21}$	$H_{20}CuP^*C_{11}$
$H_{19}GeLi^*C_{12}$	$H_{20}CuP^*C_{23}$
$H_{19}GeLi^*C_{20}$	$H_{20}Cu_2N_2^*C_{18}$
$H_{19}HgNO_4^*C_9$	$H_{20}Cu_2P_2^*C_8$
$H_{19}K^*C_{18}$	$H_{20}F_{14}HgO_4^*C_{20}$
$H_{19}K^*C_{21}$	$H_{20}F_{30}Ge_2O_2Zn^*C_{44}$
$H_{19}KO^*C_{10}$	$H_{20}FeLiOP^*C_{23}$
$H_{19}Li^*C_9$	$H_{20}FeLiPS^*C_{23}$
$H_{19}Li^*C_{10}$	$H_{20}Ge^*C_8$
$H_{19}Li^*C_{11}$	$H_{20}Ge^*C_{12}$
$H_{19}Li^*C_{14}$	$H_{20}Ge^*C_{19}$
$H_{19}Li^*C_{17}$	$H_{20}Ge^*C_{24}$
$H_{19}Li^*C_{21}$	$H_{20}GeHg^*C_8$
$H_{19}Li^*C_{23}$	$H_{20}GeO^*C_8$
$H_{19}LiNO_2P^*C_{17}$	$H_{20}Ge_2Li_2^*C_{24}$
$H_{19}LiNO_3P^*C_9$	$H_{20}HgN_2^*C_{16}$
$H_{19}LiN_2O^*C_9$	$H_{20}HgN_4O_2P_2^*C_{26}$
$H_{19}LiN_2O^*C_{11}$	$H_{20}HgO_3^*C_{18}$
$H_{19}LiN_2OP^*C_8$	$H_{20}HgSi^*C_8$
$H_{19}LiN_3OP^*C_{12}$	$H_{20}HgSn^*C_8$
$H_{19}LiO^*C_9$	$H_{20}Hg_2O_6^*C_{15}$
$H_{19}LiOS^*C_{14}$	$H_{20}Li^*C_{26}$
$H_{19}LiOSi^*C_9$	$H_{20}LiNO_3^*C_{14}$
$H_{19}LiO_2S^*C_{11}$	$H_{20}LiNO_3^*C_{15}$
$H_{19}LiO_2Si^*C_9$	$H_{20}LiO_3P^*C_{10}$
$H_{19}LiO_4Si_2^*C_9$	$H_{20}LiP^*C_9$
$H_{19}LiSi^*C_8$	$H_{20}LiSSi^*C_{16}$
$H_{19}LiSi^*C_9$	$H_{20}Li_2^*C_{10}$
$H_{19}LiSi^*C_{12}$	$H_{20}Li_2^*C_{12}$
$H_{19}LiSi^*C_{16}$	$H_{20}Li_2^*C_{18}$
$H_{19}LiSi^*C_{20}$	$H_{20}Li_2^*C_{26}$
$H_{19}LiSi_2^*C_7$	$H_{20}Li_2^*C_{28}$
$H_{19}LiSn^*C_{16}$	$H_{20}N_2Zn^*C_{16}$
$H_{19}NSi_2^*C_6$	$H_{20}Na_2^*C_{18}$
$H_{19}Na^*C_{21}$	$H_{20}OSiSn^*C_7$
$H_{19}Na^*C_{25}$	$H_{20}OSn^*C_{21}$
$H_{20}AgP^*C_{23}$	$H_{20}O_4Sn^*C_8$



- $H_{20}Pb^*C_8$   
 $H_{20}Pb^*C_{12}$   
 $H_{20}Pb^*C_{16}$   
 $H_{20}Pb^*C_{24}$   
 $H_{20}S^*C_{13}$   
 $H_{20}S^*C_{25}$   
 $H_{20}SSi^*C_{14}$   
 $H_{20}SSi^*C_{16}$   
 $H_{20}SSn^*C_{17}$   
 $H_{20}S_2^*C_{17}$   
 $H_{20}S_2^*C_{19}$   
 $H_{20}S_4^*C_{25}$   
 $H_{20}Se_4^*C_{25}$   
 $H_{20}Si^*C_{12}$   
 $H_{20}Si^*C_{21}$   
 $H_{20}Si^*C_{24}$   
 $H_{20}Si_2^*C_7$   
 $H_{20}Si_2^*C_{16}$   
 $H_{20}Sn^*C_8$   
 $H_{20}Sn^*C_9$   
 $H_{20}Sn^*C_{12}$   
 $H_{20}Sn^*C_{21}$   
 $H_{20}Sn^*C_{24}$   
 $H_{20}Sn_2^*C_7$   
 $H_{20}SrZn^*C_8$   
 $H_{21}As_2Li^*C_{25}$   
 $H_{21}AuNO_2P^*C_{23}$   
 $H_{21}AuO^*C_{28}$   
 $H_{21}B^*C_{21}$   
 $H_{21}Bi^*C_{21}$   
 $H_{21}BrHgO_2P_2^*C_{25}$   
 $H_{21}BrSn^*C_{21}$   
 $H_{21}Cl^*C_{18}$   
 $H_{21}ClPb^*C_{21}$   
 $H_{21}ClPb^*C_{22}$   
 $H_{21}ClSi^*C_{21}$   
 $H_{21}ClSn^*C_{21}$   
 $H_{21}Cs^*C_{18}$   
 $H_{21}GeHgN^*C_{10}$   
 $H_{21}GeLi^*C_9$   
 $H_{21}GeLi^*C_{21}$   
 $H_{21}HgNSi_2^*C_7$   
 $H_{21}HgN_2O_7^*C_{10}$   
 $H_{21}Hg_2O_9P^*C_{12}$   
 $H_{21}K^*C_{23}$   
 $H_{21}KSi^*C_{21}$   
 $H_{21}Li^*C_{10}$   
 $H_{21}Li^*C_{11}$   
 $H_{21}Li^*C_{15}$   
 $H_{21}Li^*C_{18}$   
 $H_{21}Li^*C_{20}$   
 $H_{21}LiN_2S_4^*C_{11}$   
 $H_{21}LiN_3OP^*C_{12}$   
 $H_{21}LiO^*C_{10}$   
 $H_{21}LiOSi^*C_{12}$   
 $H_{21}LiO_2^*C_{10}$   
 $H_{21}LiO_2^*C_{11}$   
 $H_{21}LiO_2P_2^*C_{25}$   
 $H_{21}LiP_2^*C_{25}$   
 $H_{21}LiPb^*C_{21}$   
 $H_{21}LiSb_2^*C_{25}$   
 $H_{21}LiSi^*C_9$   
 $H_{21}LiSi_4^*C_6$   
 $H_{21}LiSn^*C_9$   
 $H_{21}LiSn^*C_{21}$   
 $H_{21}Na^*C_{23}$   
 $H_{21}NaO_3Pb^*C_{21}$   
 $H_{21}NaPb^*C_{21}$   
 $H_{21}NaSn^*C_9$   
 $H_{21}Sb^*C_{21}$   
 $H_{22}AsLi^*C_{18}$   
 $H_{22}As_2^*C_{25}$   
 $H_{22}AuP^*C_{25}$   
 $H_{22}AuP^*C_{26}$   
 $H_{22}BLiO_2Si^*C_{10}$   
 $H_{22}B_{20}Hg^*C_4$   
 $H_{22}Cd^*C_{10}$   
 $H_{22}Cd^*C_{12}$   
 $H_{22}CdSi_2^*C_8$   
 $H_{22}Ge^*C_{21}$   
 $H_{22}GeO_3^*C_{21}$   
 $H_{22}Ge_2^*C_{24}$   
 $H_{22}Ge_2HgSi_2^*C_8$   
 $H_{22}Hg^*C_{10}$   
 $H_{22}Hg^*C_{12}$   
 $H_{22}Hg^*C_{28}$   
 $H_{22}HgO_2^*C_{22}$   
 $H_{22}HgO_4^*C_{13}$   
 $H_{22}HgO_8^*C_{14}$   
 $H_{22}HgS_4^*C_{26}$   
 $H_{22}HgSi_2^*C_8$   
 $H_{22}HgSi_2^*C_{10}$   
 $H_{22}HgSi_2^*C_{16}$   
 $H_{22}HgSn^*C_9$   
 $H_{22}LiN^*C_{19}$   
 $H_{22}LiNO^*C_{21}$   
 $H_{22}LiP^*C_{18}$   
 $H_{22}Li_2^*C_{28}$   
 $H_{22}Li_4^*C_{28}$   
 $H_{22}Na_2Sn^*C_{12}$   
 $H_{22}OS_2^*C_{18}$   
 $H_{22}OSn^*C_{22}$   
 $H_{22}O_2^*C_{12}$   
 $H_{22}O_2Zn^*C_{10}$

$H_{22}P_2^*C_{25}$   
 $H_{22}Pb^*C_{14}$   
 $H_{22}S^*C_{14}$   
 $H_{22}S_2^*C_{18}$   
 $H_{22}S_2^*C_{20}$   
 $H_{22}S_2^*C_{22}$   
 $H_{22}S_2Zn^*C_{10}$   
 $H_{22}Sb_2^*C_{25}$   
 $H_{22}Si^*C_{21}$   
 $H_{22}Si^*C_{25}$   
 $H_{22}Si^*C_{26}$   
 $H_{22}Si_2^*C_{16}$   
 $H_{22}Si_2^*C_{24}$   
 $H_{22}Si_2Zn^*C_8$   
 $H_{22}Sn^*C_9$   
 $H_{22}Sn^*C_{11}$   
 $H_{22}Sn^*C_{22}$   
 $H_{22}Sn^*C_{25}$   
 $H_{22}Sn_2^*C_{12}$   
 $H_{22}Zn^*C_{10}$   
 $H_{22}Zn^*C_{26}$   
 $H_{23}B^*C_{12}$   
 $H_{23}Br^*C_{12}$   
 $H_{23}ClHgO^*C_{11}$   
 $H_{23}GeLi^*C_{26}$   
 $H_{23}HgNO_4^*C_{11}$   
 $H_{23}HgNSi_2^*C_{11}$   
 $H_{23}K^*C_{12}$   
 $H_{23}K^*C_{23}$   
 $H_{23}Li^*C_{11}$   
 $H_{23}Li^*C_{20}$   
 $H_{23}LiOSi^*C_{11}$   
 $H_{23}LiO_2^*C_{11}$   
 $H_{23}LiS_2^*C_{16}$   
 $H_{23}LiSe_2^*C_{19}$   
 $H_{23}LiSi^*C_{26}$   
 $H_{23}LiSi_2^*C_{25}$   
 $H_{23}LiSi_3^*C_{12}$   
 $H_{23}LiSn^*C_{13}$   
 $H_{23}Na^*C_{12}$   
 $H_{23}Na^*C_{19}$   
 $H_{23}Na_2^*C_{12}$   
 $H_{24}As_2Hg^*C_{10}$   
 $H_{24}AuGeP^*C_{21}$   
 $H_{24}AuIP_2^*C_{28}$   
 $H_{24}Au_2N_2^*C_{18}$   
 $H_{24}B_4O_8^*C_{13}$   
 $H_{24}CuLiN_2^*C_{18}$   
 $H_{24}CuOP^*C_{10}$   
 $H_{24}Ge^*C_{26}$   
 $H_{24}GeHgN_2^*C_{13}$   
 $H_{24}GeN_3Na^*C_{18}$   
 $H_{24}HgN_2^*C_{18}$   
 $H_{24}HgN_2O_2^*C_{20}$   
 $H_{24}HgO_2^*C_{16}$   
 $H_{24}HgSn^*C_{10}$   
 $H_{24}Hg_2^*C_{36}$   
 $H_{24}Hg_3^*C_{36}$   
 $H_{24}Hg_6^*C_{36}$   
 $H_{24}Li_2^*C_{28}$   
 $H_{24}N_2Zn^*C_{18}$   
 $H_{24}OSSi^*C_{15}$   
 $H_{24}O_3Si^*C_{12}$   
 $H_{24}SSi^*C_{14}$   
 $H_{24}SSn^*C_{23}$   
 $H_{24}SSn^*C_{26}$   
 $H_{24}Si_2^*C_{21}$   
 $H_{24}Sn^*C_{12}$   
 $H_{24}Sn^*C_{13}$   
 $H_{24}Sn_2^*C_{11}$   
 $H_{25}AuCl^*C_{30}$   
 $H_{25}ClHg^*C_{12}$   
 $H_{25}CrLiO_4Si^*C_{18}$   
 $H_{25}K^*C_{12}$   
 $H_{25}KSi_2^*C_{10}$   
 $H_{25}Li^*C_{12}$   
 $H_{25}LiOSi^*C_{12}$   
 $H_{25}LiO_2^*C_{17}$   
 $H_{25}LiPbSi^*C_{22}$   
 $H_{25}LiSSi^*C_{15}$   
 $H_{25}LiSi_2^*C_{30}$   
 $H_{25}NaZn^*C_{31}$   
 $H_{26}AsLiPb^*C_{31}$   
 $H_{26}AsLiSn^*C_{31}$   
 $H_{26}B_{10}GeHg^*C_8$   
 $H_{26}ClHgNO_3^*C_{14}$   
 $H_{26}FeSn^*C_{30}$   
 $H_{26}Ge^*C_{34}$   
 $H_{26}Hg^*C_{18}$   
 $H_{26}Hg^*C_{20}$   
 $H_{26}Hg_2O_{10}P_2^*C_{13}$   
 $H_{26}Li^*C_{20}$   
 $H_{26}LiO_4P^*C_{26}$   
 $H_{26}Li_2Si^*C_{30}$   
 $H_{26}Li_4Si^*C_{30}$   
 $H_{26}Si^*C_{27}$   
 $H_{26}Si^*C_{30}$   
 $H_{26}SiSn^*C_{23}$   
 $H_{26}Si_2^*C_{10}$   
 $H_{26}Si_2^*C_{26}$   
 $H_{26}Sn^*C_{12}$   
 $H_{26}Sn_2Zn^*C_{26}$   
 $H_{27}AuNP^*C_{27}$   
 $H_{27}B^*C_{12}$

$H_{27}B^*C_{24}$	$H_{30}CdF_{30}Ge_2P_2^*C_{72}$
$H_{27}BO_2^*C_{16}$	$H_{30}CdGe_2^*C_{12}$
$H_{27}BiO_3^*C_{24}$	$H_{30}CdGe_2^*C_{36}$
$H_{27}BrSi^*C_{12}$	$H_{30}CdSi_2^*C_{12}$
$H_{27}ClPbSi^*C_{24}$	$H_{30}CdSn_2^*C_{36}$
$H_{27}GeNa^*C_{12}$	$H_{30}Cl_2GePb^*C_{37}$
$H_{27}K^*C_{19}$	$H_{30}Cl_2PbSi^*C_{37}$
$H_{27}Li^*C_{17}$	$H_{30}Cl_2Pb_2^*C_{37}$
$H_{27}LiOS^*C_{18}$	$H_{30}CoLiSn^*C_{39}$
$H_{27}LiOSe^*C_{17}$	$H_{30}Cu_2N_4^*C_{22}$
$H_{27}LiO_2^*C_{18}$	$H_{30}Cu_4Mg^*C_{36}$
$H_{27}LiO_2Si_2^*C_{12}$	$H_{30}F_2Ge_3^*C_{36}$
$H_{27}LiSi^*C_{12}$	$H_{30}F_2Ge_3Hg^*C_{36}$
$H_{27}LiSi^*C_{21}$	$H_{30}Ge^*C_{37}$
$H_{27}LiSi_3^*C_{10}$	$H_{30}GeHgSi^*C_{12}$
$H_{27}LiSi_4^*C_9$	$H_{30}GeSi^*C_{24}$
$H_{27}LiSn^*C_{12}$	$H_{30}Ge_2^*C_{12}$
$H_{27}LiSn^*C_{14}$	$H_{30}Ge_2^*C_{36}$
$H_{27}LiSn_4^*C_9$	$H_{30}Ge_2Hg^*C_{12}$
$H_{27}NSi^*C_{11}$	$H_{30}Ge_2Hg^*C_{34}$
$H_{27}NaO_3Pb^*C_{24}$	$H_{30}Ge_2Hg^*C_{36}$
$H_{27}NaSi^*C_{12}$	$H_{30}Ge_2Zn^*C_{36}$
$H_{27}NaSn^*C_{12}$	$H_{30}Hg^*C_{30}$
$H_{27}Sb^*C_{36}$	$H_{30}Hg^*C_{32}$
$H_{28}AuBrP_2^*C_{10}$	$H_{30}HgSSI_2^*C_{12}$
$H_{28}Cl_2F_3NZn^*C_{13}$	$H_{30}HgSi_2^*C_{12}$
$H_{28}Cu_4^*C_{28}$	$H_{30}HgSi_2^*C_{20}$
$H_{28}Ge^*C_{12}$	$H_{30}HgSi_2^*C_{24}$
$H_{28}Ge^*C_{28}$	$H_{30}HgSi_2^*C_{34}$
$H_{28}Hg_2Si_4^*C_{10}$	$H_{30}HgSi_2^*C_{36}$
$H_{28}LiNO^*C_{18}$	$H_{30}HgSn_2^*C_{12}$
$H_{28}LiPSi_2^*C_{19}$	$H_{30}HgSn_2^*C_{36}$
$H_{28}O_4Sn^*C_{12}$	$H_{30}LiN^*C_{14}$
$H_{28}Pb^*C_{28}$	$H_{30}LiNO^*C_{19}$
$H_{28}Si^*C_{12}$	$H_{30}O_2^*C_{38}$
$H_{28}Si_3^*C_{18}$	$H_{30}Pb_2^*C_{36}$
$H_{28}Si_3^*C_8$	$H_{30}S_2^*C_{30}$
$H_{28}Sn^*C_{12}$	$H_{30}Si^*C_{37}$
$H_{28}Sn^*C_{16}$	$H_{30}Si_2^*C_{20}$
$H_{28}Sn^*C_{33}$	$H_{30}Si_2^*C_{36}$
$H_{29}Li^*C_{14}$	$H_{30}Si_2Zn^*C_{12}$
$H_{29}Li^*C_{18}$	$H_{30}Si_4^*C_{10}$
$H_{29}LiSi_2^*C_{12}$	$H_{30}Sn_2^*C_{12}$
$H_{29}LiSn^*C_{14}$	$H_{30}Sn_2^*C_{24}$
$H_{30}AuCl_3P_2Sn^*C_{36}$	$H_{30}Sn_2^*C_{36}$
$H_{30}AuF_6P^*C_{42}$	$H_{30}Sn_2Zn^*C_{36}$
$H_{30}AuGeP^*C_{36}$	$H_{31}As_3^*C_{37}$
$H_{30}AuGe_2Li^*C_{36}$	$H_{31}B^*C_{17}$
$H_{30}AuPSi^*C_{36}$	$H_{31}B^*C_{20}$
$H_{30}Au_2F_6P_2^*C_{40}$	$H_{31}Cl_2NZn^*C_{13}$
$H_{30}Au_2I_2P_2Sn^*C_{36}$	$H_{31}CuN_2^*C_{39}$
$H_{30}Au_2N_2^*C_{39}$	

$H_{31}GeLiPb \cdot C_{37}$	$H_{36}CdN_2Si_4 \cdot C_{12}$
$H_{31}Li \cdot C_{17}$	$H_{36}F_{30}HgP_2PtSn_2 \cdot C_{78}$
$H_{31}LiPb_2 \cdot C_{37}$	$H_{36}Fe_2HgN_2 \cdot C_{28}$
$H_{31}LiSn_2 \cdot C_{37}$	$H_{36}Ge \cdot C_{16}$
$H_{31}Sb_3 \cdot C_{37}$	$H_{36}HgN_2Si_4 \cdot C_{12}$
$H_{32}CuNP \cdot C_{20}$	$H_{36}HgSn \cdot C_{16}$
$H_{32}CuNP_2 \cdot C_{38}$	$H_{36}Li_2 \cdot C_{30}$
$H_{32}GePb \cdot C_{37}$	$H_{36}Li_2Si_2 \cdot C_{40}$
$H_{32}LiNO \cdot C_{20}$	$H_{36}N_2Si_4Zn \cdot C_{12}$
$H_{32}OSn \cdot C_{14}$	$H_{36}N_2Sn_2Zn \cdot C_{36}$
$H_{32}Pb_2 \cdot C_{37}$	$H_{36}OSSn \cdot C_{17}$
$H_{32}SSn \cdot C_{14}$	$H_{36}OSn \cdot C_{18}$
$H_{32}Sn_2 \cdot C_{38}$	$H_{36}O_4Sn \cdot C_{16}$
$H_{33}B \cdot C_{18}$	$H_{36}O_4Sn \cdot C_{32}$
$H_{33}Cl_2NZn \cdot C_{14}$	$H_{36}Si_3 \cdot C_{38}$
$H_{33}Cl_2NZn \cdot C_{18}$	$H_{36}Si_5 \cdot C_{12}$
$H_{33}Cu \cdot C_{37}$	$H_{36}Si_6 \cdot C_{12}$
$H_{33}CuP_2 \cdot C_{37}$	$H_{36}Sn \cdot C_{23}$
$H_{33}F_{15}Si_3Sn_2 \cdot C_{30}$	$H_{37}AuBF_4P_2 \cdot C_{43}$
$H_{33}GeLiSi_3 \cdot C_{12}$	$H_{37}B \cdot C_{24}$
$H_{33}Ge_3Si_3Ti \cdot C_{12}$	$H_{37}CuP_2 \cdot C_{39}$
$H_{33}HgNO_2 \cdot C_{20}$	$H_{37}Li \cdot C_{18}$
$H_{33}Li \cdot C_{16}$	$H_{37}NOSn \cdot C_{16}$
$H_{33}LiSi_2 \cdot C_{18}$	$H_{37}NSn \cdot C_{21}$
$H_{33}LiSi_3Sn \cdot C_{12}$	$H_{37}NSn \cdot C_{37}$
$H_{33}NSn \cdot C_{35}$	$H_{38}AgClP_2Si_2 \cdot C_{17}$
$H_{33}NaPb \cdot C_{18}$	$H_{38}CdSi_4 \cdot C_{14}$
$H_{33}NaSn \cdot C_{18}$	$H_{38}Ge_7 \cdot C_{24}$
$H_{34}B \cdot C_{18}$	$H_{38}HgO_4 \cdot C_{22}$
$H_{34}BCu \cdot C_{36}$	$H_{38}HgSi_2 \cdot C_{14}$
$H_{34}CuN \cdot C_{39}$	$H_{38}HgSi_4 \cdot C_{14}$
$H_{34}GeO_3Zn \cdot C_{26}$	$H_{38}Li_2OSn \cdot C_{17}$
$H_{34}Hg \cdot C_{16}$	$H_{38}O_2Sn \cdot C_{17}$
$H_{34}OSn \cdot C_{15}$	$H_{38}SiSn \cdot C_{16}$
$H_{34}Si_2 \cdot C_{22}$	$H_{38}SiSn \cdot C_{17}$
$H_{34}Si_3Sn \cdot C_{12}$	$H_{38}Si_2 \cdot C_{24}$
$H_{34}Sn \cdot C_{15}$	$H_{39}AuGeP_2 \cdot C_{44}$
$H_{34}Zn \cdot C_{16}$	$H_{39}CuP_2 \cdot C_{40}$
$H_{35}B \cdot C_{18}$	$H_{39}NSn \cdot C_{18}$
$H_{35}ClGe_3 \cdot C_{42}$	$H_{39}NSn \cdot C_{21}$
$H_{35}ClGe_3Hg \cdot C_{42}$	$H_{40}Ag_4Au_2F_6N_4O_6S_2 \cdot C_{34}$
$H_{35}CuN_2O_4P_2 \cdot C_{42}$	$H_{40}Br_2Cu_4N_2 \cdot C_{36}$
$H_{35}CuO_2P_2 \cdot C_{40}$	$H_{40}Br_2Cu_6N_4 \cdot C_{32}$
$H_{35}CuP_2 \cdot C_{38}$	$H_{40}Ge_4 \cdot C_{48}$
$H_{35}LiO_5SSi \cdot C_{24}$	$H_{40}HgSi_3 \cdot C_{16}$
$H_{35}LiSi_4 \cdot C_{13}$	$H_{40}Li_2N_4 \cdot Au_2C_{36}$
$H_{35}LiSn_2 \cdot C_{15}$	$H_{40}Li_2Si_4 \cdot C_{48}$
$H_{35}NSn \cdot C_{15}$	$H_{40}Na_2Si_4 \cdot C_{48}$
$H_{36}Ag_3N_3O_3 \cdot C_{30}$	$H_{40}O_2Sn \cdot C_{18}$
$H_{36}Ag_3N_3O_3 \cdot C_{33}$	$H_{40}O_2Sn \cdot C_{20}$
$H_{36}AuBrF_{15}N \cdot C_{44}$	$H_{40}O_3Sn \cdot C_{21}$
$H_{36}Au_3N_3O_3 \cdot C_{30}$	$H_{40}Pb_2Si \cdot C_{40}$

$H_{40}Si_3 * C_{48}$   
 $H_{40}Si_4 * C_{48}$   
 $H_{40}Sn * C_{30}$   
 $H_{41}AsPb_2 * C_{49}$   
 $H_{42}Ge_2 * C_{18}$   
 $H_{42}Ge_2Hg * C_{18}$   
 $H_{42}Hg * C_{20}$   
 $H_{42}Hg * C_{36}$   
 $H_{42}HgSn_2 * C_{18}$   
 $H_{42}O_2Sn * C_{23}$   
 $H_{42}Pb_2 * C_{42}$   
 $H_{42}Si_2 * C_{42}$   
 $H_{43}LiSi_4 * C_{49}$   
 $H_{44}Cu_4Si_4 * C_{16}$   
 $H_{44}Ge_2O_3Zn * C_{42}$   
 $H_{44}OSn * C_{20}$   
 $H_{44}OSn * C_{21}$   
 $H_{44}O_2Sn * C_{24}$   
 $H_{44}O_3Sn * C_{24}$   
 $H_{44}Si_4Sn * C_{16}$   
 $H_{45}AgClP_3 * C_{54}$   
 $H_{45}AgCl_3P_3Sn * C_{54}$   
 $H_{45}AuClP_3 * C_{54}$   
 $H_{45}AuCl_3P_3Sn * C_{54}$   
 $H_{45}Au_3BF_4OP * C_{54}$   
 $H_{45}ClCuP_3 * C_{54}$   
 $H_{45}Cl_3CuP_3Sn * C_{54}$   
 $H_{45}CoSn_2 * C_{67}$   
 $H_{45}Ge_3LiSi * C_{54}$   
 $H_{45}Ge_3Ti * C_{18}$   
 $H_{45}Ge_4Li * C_{54}$   
 $H_{45}LiS_3 * C_{55}$   
 $H_{45}LiSn_4 * C_{54}$   
 $H_{45}P_3Pd * C_{54}$   
 $H_{46}GePb_2 * C_{55}$   
 $H_{46}Ge_3Si * C_{54}$   
 $H_{46}Ge_4 * C_{54}$   
 $H_{46}Pb_3 * C_{55}$   
 $H_{46}Sn_3 * C_{55}$   
 $H_{48}Ag_2Li_2N_4 * C_{36}$   
 $H_{48}Au_2Li_2N_4 * C_{36}$   
 $H_{48}Cu_2Li_2N_4 * C_{36}$   
 $H_{48}Cu_4N_4 * C_{36}$   
 $H_{48}OSiSn * C_{24}$   
 $H_{48}O_2Sn * C_{22}$   
 $H_{48}O_2Sn * C_{23}$   
 $H_{50}Ge_5 * C_{60}$   
 $H_{50}Hg * C_{24}$   
 $H_{50}Li_2Si_5 * C_{60}$   
 $H_{50}OSiSn * C_{23}$   
 $H_{50}O_2Sn * C_{23}$   
 $H_{50}P_2PbPt * C_{60}$

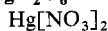
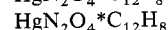
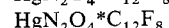
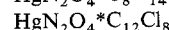
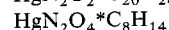
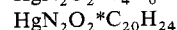
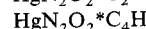
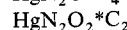
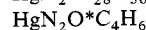
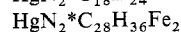
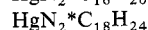
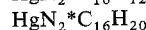
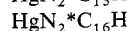
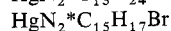
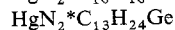
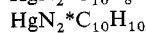
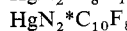
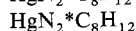
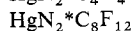
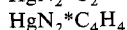
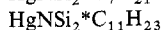
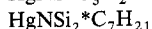
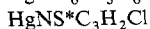
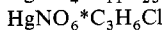
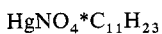
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 $H_{51}LiO_3Si_4 * C_{21}$   
 $H_{52}OSiSn * C_{24}$   
 $H_{54}CdSi_2 * C_{24}$   
 $H_{54}CdSi_6 * C_{20}$   
 $H_{54}Cu_6N_4 * C_{50}$   
 $H_{54}HgSi_2 * C_{24}$   
 $H_{54}HgSn_2 * C_{24}$   
 $H_{54}O_2Sn * C_{30}$   
 $H_{54}Si_6Zn * C_{20}$   
 $H_{54}Si_8 * C_{18}$   
 $H_{54}Sn_2 * C_{24}$   
 $H_{56}Cu_4N_4 * C_{40}$   
 $H_{56}Sn_2 * C_{26}$   
 $H_{57}HgLiO_6Si_3 * C_{21}$   
 $H_{60}AgGe * C_{72}$   
 $H_{60}Ag_4I_4P_4 * C_{72}$   
 $H_{60}Au_4Cl_3P_4Sn * C_{72}$   
 $H_{60}CdGe_2P_2Pd * C_{72}$   
 $H_{60}CuGeP_3 * C_{72}$   
 $H_{60}Cu_4I_4P_4 * C_{72}$   
 $H_{60}Ge_2HgP_2Pd * C_{72}$   
 $H_{60}HgK_2 * C_{24}$   
 $H_{60}Li_2Si_6 * C_{72}$   
 $H_{60}P_2Pb_2Pt * C_{72}$   
 $H_{60}Si_6 * C_{72}$   
 $H_{60}Sn_5 * C_{72}$   
 $H_{62}Hg * C_{34}$   
 $H_{63}Cu_3P_6 * C_{75}$   
 $H_{66}CdSi_6Sn_2 * C_{24}$   
 $H_{66}CdSn_2 * C_{30}$   
 $H_{66}Ge_2HgSi_6 * C_{24}$   
 $H_{66}HgSi_2 * C_{24}$   
 $H_{66}HgSi_6Sn_2 * C_{24}$   
 $H_{66}HgSn_2 * C_{30}$   
 $H_{66}OSi_6Sn_2 * C_{24}$   
 $H_{66}Pb_2 * C_{36}$   
 $H_{68}HgSn_2 * C_{60}$   
 $H_{72}Cu_2P_6 * C_{50}$   
 $H_{75}B * C_{36}$   
 $H_{76}Cu_2P_6 * C_{52}$   
 $H_{76}HgLi_2O_8Si_4 * C_{28}$   
 $H_{80}Cu * C_{104}$   
 $H_{80}Cu_2P_6 * C_{54}$   
 $H_{84}Cu_2P_6 * C_{54}$   
 $H_{99}Si_3Ti * C_{36}$   
 $H_{108}Cu_4I_4P_4 * C_{48}$

**Hg****Hg**Reaction with  $ArN_2X$ : 5.7.2.2.3Reaction with  $RX$ : 5.7.2.2.1 $Hg * B_2F_8$

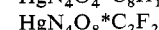
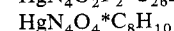
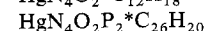
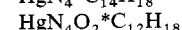
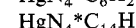
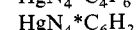
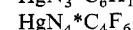
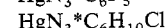
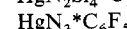
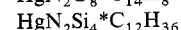
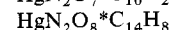
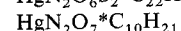
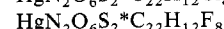
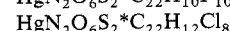
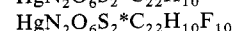
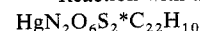
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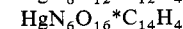
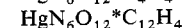
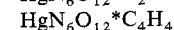
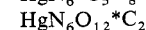
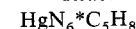
$\text{HgI}^*\text{C}_8\text{H}_9$   
 $\text{HgINO}_2^*\text{C}_6\text{H}_4$   
 $\text{HgIO}^*\text{C}_3\text{H}_5$   
 $\text{HgIO}^*\text{C}_4\text{H}_7$   
 $\text{HgIO}^*\text{C}_8\text{H}_7$   
 $\text{HgIO}^*\text{C}_9\text{H}_{11}$   
 $\text{HgISI}^*\text{Cl}_3$   
 $\text{HgI}_2$   
      $\text{HgI}_2$   
         Reaction with  $\text{R}_2\text{CN}_2$ : 5.7.2.3.5  
 $\text{HgI}_2^*\text{CH}_2$   
 $\text{HgI}_2^*\text{C}_{12}\text{H}_8$   
 $\text{HgK}_2^*\text{C}_{24}\text{H}_{60}$   
 $\text{HgLiN}^*\text{C}_8\text{H}_9\text{Br}$   
 $\text{HgLiN}^*\text{C}_9\text{H}_{11}\text{Br}$   
 $\text{HgLiN}^*\text{C}_{14}\text{H}_{13}\text{Br}$   
 $\text{HgLiO}^*\text{C}_8\text{H}_8\text{Br}$   
 $\text{HgLiO}_6\text{Si}_3^*\text{C}_{21}\text{H}_{57}$   
 $\text{HgLi}_2\text{O}_8\text{Si}_4^*\text{C}_{28}\text{H}_{76}$   
 $\text{HgMnO}_3^*\text{C}_8\text{H}_4\text{Br}$   
 $\text{HgMnO}_3^*\text{C}_8\text{H}_4\text{Cl}$   
 $\text{HgMnO}_5^*\text{C}_{15}\text{H}_9\text{ClFe}$   
 $\text{HgN}^*\text{C}_2\text{H}_2\text{Cl}$   
 $\text{HgN}^*\text{C}_3\text{H}_3\text{D}_2$   
 $\text{HgN}^*\text{C}_3\text{H}_5$   
 $\text{HgN}^*\text{C}_6\text{H}_{14}\text{Cl}$   
 $\text{HgN}^*\text{C}_7\text{F}_5$   
 $\text{HgN}^*\text{C}_8\text{H}_{16}\text{Cl}$   
 $\text{HgN}^*\text{C}_9\text{H}_5$   
 $\text{HgN}^*\text{C}_9\text{H}_{12}\text{Cl}$   
 $\text{HgN}^*\text{C}_{10}\text{H}_{21}\text{Ge}$   
 $\text{HgN}^*\text{C}_{13}\text{H}_{16}\text{ClFe}$   
 $\text{HgN}^*\text{C}_{15}\text{H}_{11}$   
 $\text{HgN}^*\text{ClH}_2$   
 $\text{HgNO}^*\text{C}_7\text{H}_5$   
 $\text{HgNO}^*\text{C}_8\text{H}_7$   
 $\text{HgNO}^*\text{C}_8\text{H}_{14}\text{Cl}$   
 $\text{HgNO}^*\text{C}_9\text{H}_{16}\text{Cl}$   
 $\text{HgNO}_2^*\text{C}_4\text{H}_5$   
 $\text{HgNO}_2^*\text{C}_3\text{H}_3\text{F}_6$   
 $\text{HgNO}_2^*\text{C}_6\text{H}_4\text{Br}$   
 $\text{HgNO}_2^*\text{C}_6\text{H}_4\text{Cl}$   
 $\text{HgNO}_2^*\text{C}_6\text{H}_{10}\text{Cl}$   
 $\text{HgNO}_2^*\text{C}_9\text{H}_{11}$   
 $\text{HgNO}_2^*\text{C}_{20}\text{H}_{33}$   
 $\text{HgNO}_3\text{S}^*\text{C}_6\text{H}_6\text{Cl}$   
 $\text{HgNO}_3^*\text{C}_6\text{H}_5$   
 $\text{HgNO}_3^*\text{C}_8\text{H}_6\text{Cl}$   
 $\text{HgNO}_3^*\text{C}_{10}\text{H}_{11}$   
 $\text{HgNO}_3^*\text{C}_{14}\text{H}_{26}\text{Cl}$   
 $\text{HgNO}_4^*\text{C}_8\text{H}_7$   
 $\text{HgNO}_4^*\text{C}_9\text{H}_{19}$



Reaction with alkenes: 5.7.2.3.3, 5.7.2.3.4



Reaction with  $\text{R}_2\text{Hg}$ : 5.7.2.3.2

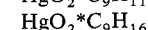
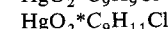
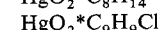
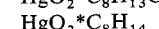
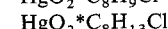
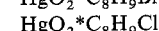
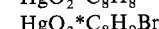
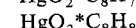
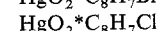
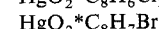
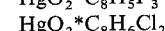
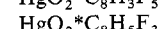
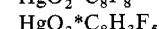
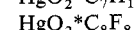
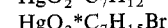
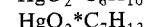
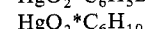
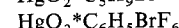
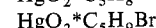
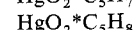
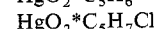
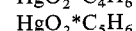
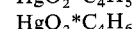
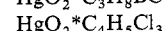
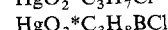
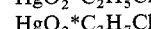
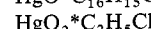
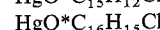
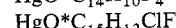
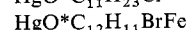
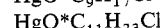
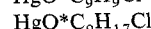
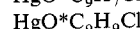
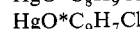
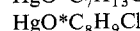
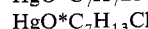
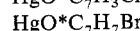
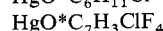
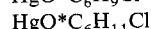
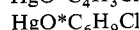
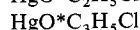
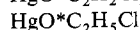
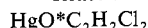


Reaction with  $\text{R}_3\text{SiX}$ : 5.7.3.2



Reaction with aliphatics: 5.7.2.3.4

Reaction with carboxylates: 5.7.2.3.7





$\text{HgO}_2 \cdot \text{C}_{10}\text{H}_{12}$   
 $\text{HgO}_2 \cdot \text{C}_{10}\text{H}_{18}$   
 $\text{HgO}_2 \cdot \text{C}_{11}\text{H}_{14}$   
 $\text{HgO}_2 \cdot \text{C}_{11}\text{H}_{19}\text{Cl}$   
 $\text{HgO}_2 \cdot \text{C}_{12}\text{H}_{10}$   
 $\text{HgO}_2 \cdot \text{C}_{12}\text{H}_{18}$   
 $\text{HgO}_2 \cdot \text{C}_{13}\text{H}_5\text{Br}_5$   
 $\text{HgO}_2 \cdot \text{C}_{13}\text{H}_5\text{Cl}_5$   
 $\text{HgO}_2 \cdot \text{C}_{13}\text{H}_5\text{F}_5$   
 $\text{HgO}_2 \cdot \text{C}_{14}\text{H}_6\text{Br}_8$   
 $\text{HgO}_2 \cdot \text{C}_{14}\text{H}_6\text{F}_8$   
 $\text{HgO}_2 \cdot \text{C}_{14}\text{H}_7\text{Cl}_5$   
 $\text{HgO}_2 \cdot \text{C}_{14}\text{H}_{14}$   
 $\text{HgO}_2 \cdot \text{C}_{16}\text{H}_{14}$   
 $\text{HgO}_2 \cdot \text{C}_{16}\text{H}_{15}\text{Cl}$   
 $\text{HgO}_2 \cdot \text{C}_{16}\text{H}_{24}$   
 $\text{HgO}_2 \cdot \text{C}_{18}\text{H}_{14}$   
 $\text{HgO}_2 \cdot \text{C}_{18}\text{H}_{18}$   
 $\text{HgO}_2 \cdot \text{C}_{22}\text{H}_{22}$   
 $\text{HgO}_2\text{P}_2 \cdot \text{C}_{25}\text{H}_{21}\text{Br}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_6\text{H}_4\text{Cl}_2$   
 $\text{HgO}_2\text{S} \cdot \text{C}_6\text{H}_{11}\text{Cl}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_6\text{H}_{13}\text{Cl}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_7\text{H}_7\text{Cl}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_8\text{H}_{10}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_{12}\text{H}_8\text{Cl}_2$   
 $\text{HgO}_2\text{S} \cdot \text{C}_{12}\text{H}_{10}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_{12}\text{H}_{13}\text{Cl}$   
 $\text{HgO}_2\text{S} \cdot \text{C}_{13}\text{H}_{12}$   
 $\text{HgO}_2\text{Si} \cdot \text{C}_7\text{H}_{12}$   
 $\text{HgO}_3 \cdot \text{C}_5\text{H}_8\text{D}_2$   
 $\text{HgO}_3 \cdot \text{C}_7\text{H}_{12}$   
 $\text{HgO}_3 \cdot \text{C}_8\text{H}_9$   
 $\text{HgO}_3 \cdot \text{C}_8\text{H}_{13}\text{Cl}$   
 $\text{HgO}_3 \cdot \text{C}_8\text{H}_{14}$   
 $\text{HgO}_3 \cdot \text{C}_9\text{H}_5\text{ClCr}$   
 $\text{HgO}_3 \cdot \text{C}_9\text{H}_{10}$   
 $\text{HgO}_3 \cdot \text{C}_9\text{H}_{15}\text{F}_3$   
 $\text{HgO}_3 \cdot \text{C}_9\text{H}_{18}$   
 $\text{HgO}_3 \cdot \text{C}_{15}\text{H}_{10}\text{F}_4$   
 $\text{HgO}_3 \cdot \text{C}_{18}\text{H}_{20}$   
 $\text{HgO}_3\text{Re} \cdot \text{C}_6\text{H}_4\text{Br}$   
 $\text{HgO}_3\text{Re} \cdot \text{C}_8\text{H}_4\text{Cl}$   
 $\text{HgO}_3\text{S} \cdot \text{C}_{12}\text{H}_2\text{F}_8$   
 $\text{HgO}_4 \cdot \text{C}_4\text{F}_6$   
 $\text{HgO}_4 \cdot \text{C}_4\text{H}_6$   
 $\text{HgO}_4 \cdot \text{C}_6\text{H}_{10}$   
 $\text{HgO}_4 \cdot \text{C}_7\text{H}_{12}$   
 $\text{HgO}_4 \cdot \text{C}_8\text{F}_4$   
 $\text{HgO}_4 \cdot \text{C}_8\text{H}_{12}$   
 $\text{HgO}_4 \cdot \text{C}_{10}\text{F}_{18}$   
 $\text{HgO}_4 \cdot \text{C}_{10}\text{H}_{14}$

$\text{HgO}_4 \cdot \text{C}_{13}\text{H}_{22}$   
 $\text{HgO}_4 \cdot \text{C}_{14}\text{Br}_8\text{Cl}_2$   
 $\text{HgO}_4 \cdot \text{C}_{14}\text{Br}_8\text{F}_2$   
 $\text{HgO}_4 \cdot \text{C}_{14}\text{Cl}_{10}$   
 $\text{HgO}_4 \cdot \text{C}_{14}\text{F}_{10}$   
 $\text{HgO}_4 \cdot \text{C}_{14}\text{H}_6\text{F}_4$   
 $\text{HgO}_4 \cdot \text{C}_{16}\text{H}_{14}$   
 $\text{HgO}_4 \cdot \text{C}_{17}\text{H}_{16}$   
 $\text{HgO}_4 \cdot \text{C}_{20}\text{H}_{20}\text{F}_{14}$   
 $\text{HgO}_4 \cdot \text{C}_{22}\text{H}_{38}$   
 $\text{HgO}_4\text{S}_2 \cdot \text{C}_{12}\text{H}_8\text{F}_2$   
 $\text{HgO}_4\text{S}_2 \cdot \text{C}_{12}\text{H}_{10}$   
 $\text{HgO}_4\text{S}_2 \cdot \text{C}_{14}\text{H}_{14}$   
 $\text{HgO}_5 \cdot \text{C}_3\text{H}_7\text{Cl}$   
 $\text{HgO}_6 \cdot \text{C}_{12}\text{H}_{18}$   
 $\text{HgO}_6 \cdot \text{C}_{16}\text{H}_6\text{Br}_8$   
 $\text{HgO}_6 \cdot \text{C}_{18}\text{H}_{10}\text{Cr}_2$   
 $\text{HgO}_6\text{S}_2 \cdot \text{C}_{15}\text{H}_{14}$   
 $\text{HgO}_8 \cdot \text{C}_{10}\text{H}_{14}$   
 $\text{HgO}_8 \cdot \text{C}_{14}\text{H}_{22}$   
 $\text{HgO}_8\text{S}_2 \cdot \text{C}_{12}\text{H}_4\text{Cl}_{10}$   
 $\text{HgO}_8\text{S}_2 \cdot \text{C}_{12}\text{H}_4\text{F}_{10}$   
 $\text{HgO}_8\text{S}_2 \cdot \text{C}_{12}\text{H}_6\text{Cl}_8$   
 $\text{HgO}_8\text{S}_2 \cdot \text{C}_{12}\text{H}_6\text{F}_8$   
 $\text{HgP} \cdot \text{C}_{19}\text{H}_{16}\text{Br}$   
 $\text{HgP} \cdot \text{C}_{19}\text{H}_{16}\text{Br}_2\text{Cu}$   
 $\text{HgP}_2\text{Pd} \cdot \text{C}_{72}\text{H}_{60}\text{Ge}_2$   
 $\text{HgP}_2\text{PtSn}_2 \cdot \text{C}_{78}\text{H}_{36}\text{F}_{30}$   
 $\text{HgPb} \cdot \text{C}_{18}\text{H}_{15}\text{Cl}$   
 $\text{HgPb} \cdot \text{C}_{25}\text{H}_{20}\text{Cl}_2$   
**HgPb<sub>2</sub>**  
     HgPb<sub>2</sub>  
         Formation: 5.7.6.1.2  
 $\text{HgPr} \cdot \text{C}_{90}\text{F}_{75}\text{Ge}_5$   
 $\text{HgS} \cdot \text{C}_4\text{H}_3\text{Cl}$   
 $\text{HgSSi}_2 \cdot \text{C}_{12}\text{H}_{30}$   
 $\text{HgS}_2 \cdot \text{C}_{14}\text{H}_{14}$   
 $\text{HgS}_2 \cdot \text{C}_{16}\text{H}_{10}$   
 $\text{HgS}_4 \cdot \text{C}_{26}\text{H}_{22}$   
 $\text{HgSi} \cdot \text{BrCl}_3$   
 $\text{HgSi} \cdot \text{C}_2\text{H}_5\text{Cl}_3$   
 $\text{HgSi} \cdot \text{C}_2\text{H}_6$   
 $\text{HgSi} \cdot \text{C}_3\text{H}_9\text{Cl}_3\text{Ge}$   
 $\text{HgSi} \cdot \text{C}_4\text{H}_{11}\text{Cl}$   
 $\text{HgSi} \cdot \text{C}_4\text{H}_{11}\text{Cl}_3\text{Ge}$   
 $\text{HgSi} \cdot \text{C}_6\text{H}_{12}$   
 $\text{HgSi} \cdot \text{C}_6\text{H}_{18}\text{Ge}$   
 $\text{HgSi} \cdot \text{C}_8\text{H}_{17}\text{Cl}$   
 $\text{HgSi} \cdot \text{C}_8\text{H}_{20}$   
 $\text{HgSi} \cdot \text{C}_{12}\text{H}_{30}\text{Ge}$   
 $\text{HgSiSn} \cdot \text{C}_6\text{H}_{18}$   
 $\text{HgSi}_2 \cdot \text{C}_2\text{H}_6\text{Cl}_4$

HgSi <sub>2</sub> *C <sub>3</sub> H <sub>9</sub> Cl <sub>3</sub>	Hg <sub>2</sub> *C <sub>36</sub> H <sub>24</sub>
HgSi <sub>2</sub> *C <sub>3</sub> H <sub>12</sub>	Hg <sub>2</sub> *Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub>	Hg <sub>2</sub> *F <sub>2</sub>
HgSi <sub>2</sub> *C <sub>4</sub> H <sub>14</sub>	Hg <sub>2</sub> I <sub>2</sub> *CH <sub>2</sub>
HgSi <sub>2</sub> *C <sub>6</sub> H <sub>16</sub>	Hg <sub>2</sub> N* <sup>*</sup> C <sub>13</sub> H <sub>15</sub> Br <sub>2</sub>
HgSi <sub>2</sub> *C <sub>6</sub> H <sub>18</sub>	Hg <sub>2</sub> NO <sub>4</sub> *C <sub>10</sub> H <sub>11</sub>
HgSi <sub>2</sub> *C <sub>7</sub> H <sub>19</sub> Br	Hg <sub>2</sub> N <sub>2</sub> *C <sub>3</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>8</sub> H <sub>22</sub>	Hg <sub>2</sub> O* <sup>*</sup> C <sub>2</sub> H <sub>6</sub>
HgSi <sub>2</sub> *C <sub>8</sub> H <sub>22</sub> Ge <sub>2</sub>	Hg <sub>2</sub> O* <sup>*</sup> C <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>10</sub> H <sub>22</sub>	Hg <sub>2</sub> O* <sup>*</sup> C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>12</sub> H <sub>30</sub>	Hg <sub>2</sub> O* <sup>*</sup> C <sub>6</sub> H <sub>12</sub> Br <sub>2</sub>
HgSi <sub>2</sub> *C <sub>14</sub> H <sub>38</sub>	Hg <sub>2</sub> O* <sup>*</sup> C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>16</sub> H <sub>12</sub> F <sub>10</sub>	Hg <sub>2</sub> O* <sup>*</sup> C <sub>15</sub> H <sub>11</sub> Cl <sub>2</sub> F
HgSi <sub>2</sub> *C <sub>16</sub> H <sub>22</sub>	Hg <sub>2</sub> O <sub>2</sub> * <sup>*</sup> C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>20</sub> H <sub>30</sub>	Hg <sub>2</sub> O <sub>2</sub> * <sup>*</sup> C <sub>6</sub> H <sub>12</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>24</sub> H <sub>30</sub>	Hg <sub>2</sub> O <sub>2</sub> * <sup>*</sup> C <sub>10</sub> H <sub>6</sub> F <sub>4</sub>
HgSi <sub>2</sub> *C <sub>24</sub> H <sub>54</sub>	Hg <sub>2</sub> O <sub>2</sub> * <sup>*</sup> C <sub>11</sub> H <sub>18</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>24</sub> H <sub>66</sub>	Hg <sub>2</sub> O <sub>2</sub> * <sup>*</sup> C <sub>16</sub> H <sub>16</sub> Cl <sub>2</sub>
HgSi <sub>2</sub> *C <sub>34</sub> H <sub>30</sub>	Hg <sub>2</sub> O <sub>2</sub> S* <sup>*</sup> C <sub>10</sub> H <sub>11</sub> Br
HgSi <sub>2</sub> *C <sub>36</sub> H <sub>30</sub>	Hg <sub>2</sub> O <sub>4</sub> * <sup>*</sup> C <sub>9</sub> H <sub>11</sub>
HgSi <sub>2</sub> *Cl <sub>6</sub>	Hg <sub>2</sub> O <sub>4</sub> * <sup>*</sup> C <sub>10</sub> H <sub>10</sub>
HgSi <sub>2</sub> *H <sub>6</sub>	Hg <sub>2</sub> O <sub>6</sub> * <sup>*</sup> C <sub>15</sub> H <sub>20</sub>
HgSi <sub>3</sub> * <sup>*</sup> C <sub>16</sub> H <sub>40</sub>	Hg <sub>2</sub> O <sub>6</sub> S <sub>2</sub> * <sup>*</sup> C <sub>18</sub> H <sub>2</sub> Cl <sub>12</sub>
HgSi <sub>4</sub> * <sup>*</sup> C <sub>14</sub> H <sub>38</sub>	Hg <sub>2</sub> O <sub>6</sub> S <sub>2</sub> * <sup>*</sup> C <sub>18</sub> H <sub>2</sub> F <sub>12</sub>
HgSi <sub>6</sub> *C <sub>24</sub> H <sub>66</sub> Ge <sub>2</sub>	Hg <sub>2</sub> O <sub>8</sub> S <sub>2</sub> * <sup>*</sup> C <sub>17</sub> H <sub>16</sub>
HgSi <sub>6</sub> Sn <sub>2</sub> *C <sub>24</sub> H <sub>66</sub>	Hg <sub>2</sub> O <sub>9</sub> P* <sup>*</sup> C <sub>12</sub> H <sub>21</sub>
HgSn*C <sub>6</sub> H <sub>14</sub> Cl <sub>2</sub>	Hg <sub>2</sub> O <sub>10</sub> P <sub>2</sub> * <sup>*</sup> C <sub>13</sub> H <sub>26</sub>
HgSn*C <sub>7</sub> H <sub>18</sub>	Hg <sub>2</sub> S* <sup>*</sup> C <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub>
HgSn*C <sub>8</sub> H <sub>20</sub>	Hg <sub>2</sub> Si <sub>4</sub> * <sup>*</sup> C <sub>10</sub> H <sub>28</sub>
HgSn*C <sub>9</sub> H <sub>22</sub>	Hg <sub>3</sub> *CHCl <sub>3</sub>
HgSn*C <sub>10</sub> H <sub>24</sub>	Hg <sub>3</sub> *C <sub>36</sub> H <sub>24</sub>
HgSn*C <sub>16</sub> H <sub>36</sub>	Hg <sub>3</sub> N* <sup>*</sup> C <sub>5</sub> H <sub>9</sub>
HgSn*C <sub>18</sub> H <sub>15</sub> Cl	Hg <sub>3</sub> NO <sub>3</sub> * <sup>*</sup> C <sub>8</sub> H <sub>9</sub>
HgSn*C <sub>36</sub> F <sub>30</sub> Ge	Hg <sub>3</sub> O <sub>4</sub> * <sup>*</sup> C <sub>6</sub> H <sub>15</sub> As
HgSn <sub>2</sub> *C <sub>6</sub> H <sub>18</sub>	Hg <sub>3</sub> O <sub>4</sub> * <sup>*</sup> C <sub>8</sub> H <sub>10</sub> Cl <sub>4</sub>
HgSn <sub>2</sub> *C <sub>12</sub> H <sub>30</sub>	Hg <sub>3</sub> O <sub>4</sub> P* <sup>*</sup> C <sub>3</sub> H <sub>9</sub>
HgSn <sub>2</sub> *C <sub>18</sub> H <sub>42</sub>	Hg <sub>3</sub> O <sub>4</sub> P* <sup>*</sup> C <sub>6</sub> H <sub>15</sub>
HgSn <sub>2</sub> *C <sub>24</sub> H <sub>54</sub>	Hg <sub>4</sub> *CCl <sub>4</sub>
HgSn <sub>2</sub> *C <sub>30</sub> H <sub>66</sub>	Hg <sub>5</sub> NO <sub>12</sub> * <sup>*</sup> C <sub>16</sub> F <sub>15</sub>
HgSn <sub>2</sub> *C <sub>36</sub> F <sub>30</sub>	Hg <sub>5</sub> O <sub>10</sub> * <sup>*</sup> C <sub>16</sub> HF <sub>15</sub>
HgSn <sub>2</sub> *C <sub>36</sub> H <sub>30</sub>	Hg <sub>5</sub> O <sub>10</sub> * <sup>*</sup> C <sub>17</sub> H <sub>3</sub> F <sub>15</sub>
HgSn <sub>2</sub> *C <sub>60</sub> H <sub>68</sub>	Hg <sub>6</sub> * <sup>*</sup> C <sub>36</sub> H <sub>24</sub>
Hg <sub>2</sub> *CH <sub>2</sub> Cl <sub>2</sub>	Hg <sub>6</sub> O <sub>12</sub> * <sup>*</sup> C <sub>18</sub> F <sub>18</sub>
Hg <sub>2</sub> *C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub>	Hg <sub>8</sub> O <sub>16</sub> * <sup>*</sup> C <sub>26</sub> F <sub>24</sub>
Hg <sub>2</sub> *C <sub>4</sub> H <sub>6</sub>	I*CD <sub>3</sub> Hg
Hg <sub>2</sub> *C <sub>5</sub> H <sub>10</sub> Br <sub>2</sub>	I*CF <sub>3</sub> Hg
Hg <sub>2</sub> *C <sub>6</sub> Br <sub>2</sub> F <sub>4</sub>	I*CH <sub>3</sub> Cd
Hg <sub>2</sub> *C <sub>6</sub> Cl <sub>2</sub> F <sub>4</sub>	I*CH <sub>3</sub> Hg
Hg <sub>2</sub> *C <sub>7</sub> H <sub>3</sub> Cl <sub>2</sub> F <sub>3</sub>	I*C <sub>2</sub> H <sub>5</sub> Cd
Hg <sub>2</sub> *C <sub>8</sub> H <sub>16</sub>	I*C <sub>4</sub> H <sub>9</sub> Hg
Hg <sub>2</sub> *C <sub>10</sub> H <sub>8</sub> Cl <sub>2</sub> Fe	I*C <sub>6</sub> H <sub>5</sub> Cd
Hg <sub>2</sub> *C <sub>16</sub> H <sub>14</sub> Cl <sub>2</sub>	I*C <sub>6</sub> H <sub>5</sub> Hg

- $I^*C_7H_5Hg$   
 $I^*C_8H_5Hg$   
 $ILiNS^*C_3H$   
 $ILiS^*C_4H_2$   
 $IMg^*CH_3$   
 $INO_2^*C_6H_4Hg$   
 $IO^*C_3H_5Hg$   
 $IO^*C_4H_7Hg$   
 $IO^*C_8H_7Hg$   
 $IO^*C_9H_{11}Hg$   
 $IP_2^*C_{28}H_{24}Au$   
 $ISi^*Cl_3Hg$   
 $IZn^*C_2H_5$   
 $IZn^*C_3F_7$   
 $IZn^*C_7H_7$   
 $I_2^*CH_2Hg$   
 $I_2^*CH_2Hg_2$   
 $I_2^*C_2H_4Cd$   
 $I_2^*C_{12}H_8Hg$   
 $I_2^*Cd$   
 $I_2^*Ge$   
 $I_2^*Hg$   
 $I_2P_2Sn^*C_{36}H_{30}Au_2$   
 $I_2Zn$   
 $ZnI_2$   
 Reaction with  $RAg$ : 5.7.2.3.1  
 Reaction with  $CH_2N_2$ : 5.7.2.3.5  
 $I_2Zn^*CH_2$   
 $I_2Zn^*C_2H_4$   
 $I_2Zn_2^*CH_2$   
 $I_4P_4^*C_{48}H_{108}Cu_4$   
 $I_4P_4^*C_{72}H_{60}Ag_4$   
 $I_4P_4^*C_{72}H_{60}Cu_4$   
 $I_4Zn_2^*C_8H_6$   
**K**  
**K**  
 Reaction with  $Ph_6Pb_2$ : 5.5.7.2.1  
 Reaction with  $R_3GeLi$ : 5.5.5.7  
 Reaction with  $R_4Pb$ : 5.5.7.3  
 $K^*CH_3$   
 $K^*C_3H_5$   
 $K^*C_3H_7$   
 $K^*C_4H_2Au$   
 $K^*C_4H_9$   
 $K^*C_5H_7$   
 $K^*C_5H_{11}$   
 $K^*C_6H_5$   
 $K^*C_6H_6$   
 $K^*C_6H_{15}Ge$   
 $K^*C_7H_7$   
 $K^*C_8$   
 $K^*C_8H_5$   
 $K^*C_8H_{17}$   
 $K^*C_9H_9$   
 $K^*C_9H_{10}$   
 $K^*C_9H_{11}$   
 $K^*C_{10}H_8$   
 $K^*C_{10}H_{13}$   
 $K^*C_{11}H_9$   
 $K^*C_{11}H_{15}$   
 $K^*C_{12}H_{10}$   
 $K^*C_{12}H_{23}$   
 $K^*C_{12}H_{25}$   
 $K^*C_{13}H_9$   
 $K^*C_{13}H_{11}$   
 $K^*C_{13}H_{15}$   
 $K^*C_{14}H_{10}$   
 $K^*C_{14}H_{13}$   
 $K^*C_{15}H_{13}$   
 $K^*C_{18}H_{15}Ge$   
 $K^*C_{18}H_{19}$   
 $K^*C_{19}H_{13}$   
 $K^*C_{19}H_{15}$   
 $K^*C_{19}H_{27}$   
 $K^*C_{21}H_{19}$   
 $K^*C_{23}H_{21}$   
 $K^*C_{23}H_{23}$   
 $K^*C_{24}$   
 $K^*C_{36}$   
 $K^*C_{48}$   
 $K^*C_{60}$   
 $K^*Cl$   
 $K^*F$   
 $K^*Ge$   
 $K^*GeH_3$   
 $K^*H$   
 $KLiO^*C_3H_4$   
 $KN^*C$   
 $KN^*C_6H_{14}$   
**KNa**  
 Na-K  
 Reaction with  $R_4Pb$ : 5.5.7.3  
 $KO^*CH_3$   
 $KO^*C_4H_9$   
 $KO^*C_5H_7$   
 $KO^*C_{10}H_{19}$   
 $KO^*C_{13}H_9$   
 $KO^*H$   
 $KOS^*C_2H_5$   
 $KO_2^*C_{15}H_{11}$   
**KPb**  
**KPb**  
 Formation: 5.5.7.1.1  
 $KPb^*C_3H_9$

$\text{KPb}^*\text{C}_{18}\text{H}_{15}$	$\text{Li}^*\text{CBr}_2\text{F}$
$\text{KPb}_2$	$\text{Li}^*\text{CBr}_3$
$\text{KPb}_2$	$\text{Li}^*\text{CCl}_2\text{F}$
Formation: 5.5.7.1.1	$\text{Li}^*\text{CCl}_3$
<b>KS</b>	$\text{Li}^*\text{CHBrCl}$
$\text{KSi}$	$\text{Li}^*\text{CHBr}_2$
Formation: 5.5.4.1	$\text{Li}^*\text{CHCl}_2$
$\text{KSi}^*\text{C}_3\text{H}_9$	$\text{Li}^*\text{CH}_2\text{Br}$
$\text{KSi}^*\text{C}_4\text{H}_{11}$	$\text{Li}^*\text{CH}_2\text{Cl}$
$\text{KSi}^*\text{C}_6\text{H}_{15}$	$\text{Li}^*\text{CH}_3$
$\text{KSi}^*\text{C}_{18}\text{H}_{15}$	$\text{Li}^*\text{C}_2\text{Cl}_3$
$\text{KSi}^*\text{C}_{21}\text{H}_{21}$	$\text{Li}^*\text{C}_2\text{F}_3$
$\text{KSi}^*\text{H}_3$	$\text{Li}^*\text{C}_2\text{H}$
$\text{KSi}_2^*\text{C}_{10}\text{H}_{25}$	$\text{Li}^*\text{C}_2\text{HCl}_2$
<b>KSn</b>	$\text{Li}^*\text{C}_2\text{HF}_2$
$\text{KSn}$	$\text{Li}^*\text{C}_2\text{H}_2\text{Cl}$
Formation: 5.5.6.1.3	$\text{Li}^*\text{C}_2\text{H}_3$
$\text{KSn}^*\text{C}_3\text{H}_9$	$\text{Li}^*\text{C}_2\text{H}_3\text{Cl}_2$
$\text{KSn}^*\text{C}_{18}\text{H}_{15}$	$\text{Li}^*\text{C}_2\text{H}_5$
<b>KSn<sub>2</sub></b>	$\text{Li}^*\text{C}_2\text{H}_6\text{Au}$
$\text{KSn}_2$	$\text{Li}^*\text{C}_2\text{H}_6\text{Cu}$
Formation: 5.5.6.1.3	$\text{Li}^*\text{C}_2\text{H}_7\text{Ge}$
<b>KSn<sub>4</sub></b>	$\text{Li}^*\text{C}_3\text{F}_7$
$\text{KSn}_4$	$\text{Li}^*\text{C}_3\text{H}_2\text{F}_3$
Formation: 5.5.6.1.3	$\text{Li}^*\text{C}_3\text{H}_3$
$\text{K}_2^*\text{C}_6\text{H}_8$	$\text{Li}^*\text{C}_3\text{H}_3\text{Cl}_2$
$\text{K}_2^*\text{C}_8\text{H}_8$	$\text{Li}^*\text{C}_3\text{H}_3\text{F}_2$
$\text{K}_2^*\text{C}_8\text{H}_{18}\text{Ge}$	$\text{Li}^*\text{C}_3\text{H}_4\text{Cl}$
$\text{K}_2^*\text{C}_9\text{H}_{10}$	$\text{Li}^*\text{C}_3\text{H}_5$
$\text{K}_2^*\text{C}_{10}\text{H}_8$	$\text{Li}^*\text{C}_3\text{H}_7$
$\text{K}_2^*\text{C}_{10}\text{H}_8\text{Fe}$	$\text{Li}^*\text{C}_3\text{H}_9\text{Ge}$
$\text{K}_2^*\text{C}_{12}\text{H}_{10}$	$\text{Li}^*\text{C}_4\text{H}_5$
$\text{K}_2^*\text{C}_{14}\text{H}_{10}$	$\text{Li}^*\text{C}_4\text{H}_6\text{Cl}$
$\text{K}_2^*\text{C}_{15}\text{H}_{15}$	$\text{Li}^*\text{C}_4\text{H}_7$
$\text{K}_2^*\text{C}_{18}\text{H}_{14}$	$\text{Li}^*\text{C}_4\text{H}_9$
$\text{K}_2^*\text{C}_{19}\text{H}_{15}$	$\text{Li}^*\text{C}_5\text{F}_{11}$
$\text{K}_2^*\text{C}_{24}\text{H}_{60}\text{Hg}$	$\text{Li}^*\text{C}_5\text{H}_5$
$\text{K}_2\text{O}_3^*\text{C}$	$\text{Li}^*\text{C}_5\text{H}_6\text{Br}$
<b>K<sub>2</sub>Sn</b>	$\text{Li}^*\text{C}_5\text{H}_7$
$\text{K}_2\text{Sn}$	$\text{Li}^*\text{C}_5\text{H}_7\text{D}_2$
Formation: 5.5.6.1.3	$\text{Li}^*\text{C}_5\text{H}_9$
$\text{K}_4^*\text{C}_{18}\text{H}_{14}$	$\text{Li}^*\text{C}_5\text{H}_9\text{Br}_2$
<b>Li</b>	$\text{Li}^*\text{C}_5\text{H}_{10}\text{Br}$
<b>Li</b>	$\text{Li}^*\text{C}_5\text{H}_{11}$
Reaction with $\text{R}_4\text{Pb}$ : 5.5.7.3	$\text{Li}^*\text{C}_6$
Reaction with $\text{R}_6\text{Pb}_2$ : 5.5.7.2.1	$\text{Li}^*\text{C}_6\text{BrF}_4$
Reaction with $\text{R}_3\text{PbX}$ : 5.5.7.4	$\text{Li}^*\text{C}_6\text{Br}_5$
Reaction with $\text{Ph}_3\text{PbX}_2$ : 5.5.7.4	$\text{Li}^*\text{C}_6\text{Cl}_5$
Reaction with $\text{C}_2\text{H}_2$ : 5.5.2.1	$\text{Li}^*\text{C}_6\text{F}_5$
Reaction with elemental carbon: 5.5.2.1	$\text{Li}^*\text{C}_6\text{F}_9$
Reaction with organohalides: 5.5.2.2.1	$\text{Li}^*\text{C}_6\text{HCl}_4$
$\text{Li}^*\text{CBrCl}_2$	$\text{Li}^*\text{C}_6\text{H}_2\text{Cl}_3$

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Li*C <sub>6</sub> H <sub>4</sub> Br	Li*C <sub>10</sub> H <sub>13</sub>
Li*C <sub>6</sub> H <sub>4</sub> Cl	Li*C <sub>10</sub> H <sub>14</sub> As
Li*C <sub>6</sub> H <sub>4</sub> F	Li*C <sub>10</sub> H <sub>15</sub>
Li*C <sub>6</sub> H <sub>5</sub>	Li*C <sub>10</sub> H <sub>17</sub>
Li*C <sub>6</sub> H <sub>6</sub>	Li*C <sub>10</sub> H <sub>19</sub>
Li*C <sub>6</sub> H <sub>7</sub>	Li*C <sub>10</sub> H <sub>21</sub>
Li*C <sub>6</sub> H <sub>7</sub> Ge	Li*C <sub>11</sub> H <sub>10</sub> Cl
Li*C <sub>6</sub> H <sub>9</sub>	Li*C <sub>11</sub> H <sub>11</sub> Fe
Li*C <sub>6</sub> H <sub>9</sub> Ge	Li*C <sub>11</sub> H <sub>13</sub>
Li*C <sub>6</sub> H <sub>11</sub>	Li*C <sub>11</sub> H <sub>19</sub>
Li*C <sub>6</sub> H <sub>13</sub>	Li*C <sub>11</sub> H <sub>21</sub>
Li*C <sub>6</sub> H <sub>15</sub> Ge	Li*C <sub>11</sub> H <sub>23</sub>
Li*C <sub>7</sub> BrCl <sub>6</sub>	Li*C <sub>12</sub>
Li*C <sub>7</sub> F <sub>15</sub>	Li*C <sub>12</sub> CuF <sub>10</sub>
Li*C <sub>7</sub> H <sub>4</sub> F <sub>3</sub>	Li*C <sub>12</sub> H <sub>8</sub>
Li*C <sub>7</sub> H <sub>5</sub> Br <sub>2</sub>	Li*C <sub>12</sub> H <sub>9</sub>
Li*C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub>	Li*C <sub>12</sub> H <sub>10</sub>
Li*C <sub>7</sub> H <sub>6</sub> F	Li*C <sub>12</sub> H <sub>10</sub> As
Li*C <sub>7</sub> H <sub>7</sub>	Li*C <sub>12</sub> H <sub>11</sub> Ge
Li*C <sub>7</sub> H <sub>8</sub> Cl	Li*C <sub>12</sub> H <sub>19</sub> Ge
Li*C <sub>7</sub> H <sub>11</sub>	Li*C <sub>12</sub> H <sub>25</sub>
Li*C <sub>7</sub> H <sub>13</sub>	Li*C <sub>13</sub> H <sub>9</sub>
Li*C <sub>7</sub> H <sub>15</sub>	Li*C <sub>13</sub> H <sub>10</sub>
Li*C <sub>7</sub> H <sub>17</sub> Ge	Li*C <sub>13</sub> H <sub>11</sub>
Li*C <sub>8</sub> H <sub>3</sub> F <sub>6</sub>	Li*C <sub>13</sub> H <sub>12</sub> As
Li*C <sub>8</sub> H <sub>5</sub>	Li*C <sub>14</sub> H <sub>10</sub>
Li*C <sub>8</sub> H <sub>6</sub> Cl	Li*C <sub>14</sub> H <sub>10</sub> Br
Li*C <sub>8</sub> H <sub>7</sub>	Li*C <sub>14</sub> H <sub>11</sub>
Li*C <sub>8</sub> H <sub>8</sub> Br	Li*C <sub>14</sub> H <sub>12</sub>
Li*C <sub>8</sub> H <sub>9</sub>	Li*C <sub>14</sub> H <sub>13</sub>
Li*C <sub>8</sub> H <sub>10</sub>	Li*C <sub>14</sub> H <sub>19</sub>
Li*C <sub>8</sub> H <sub>11</sub>	Li*C <sub>14</sub> H <sub>29</sub>
Li*C <sub>8</sub> H <sub>11</sub> Ge	Li*C <sub>15</sub> H <sub>9</sub>
Li*C <sub>8</sub> H <sub>13</sub>	Li*C <sub>15</sub> H <sub>13</sub>
Li*C <sub>8</sub> H <sub>15</sub>	Li*C <sub>15</sub> H <sub>15</sub>
Li*C <sub>8</sub> H <sub>17</sub>	Li*C <sub>15</sub> H <sub>21</sub>
Li*C <sub>9</sub> H <sub>5</sub> F <sub>4</sub>	Li*C <sub>16</sub> H <sub>15</sub>
Li*C <sub>9</sub> H <sub>7</sub>	Li*C <sub>16</sub> H <sub>17</sub>
Li*C <sub>9</sub> H <sub>8</sub> F	Li*C <sub>16</sub> H <sub>18</sub> As
Li*C <sub>9</sub> H <sub>9</sub>	Li*C <sub>16</sub> H <sub>33</sub>
Li*C <sub>9</sub> H <sub>10</sub>	Li*C <sub>17</sub> H <sub>15</sub>
Li*C <sub>9</sub> H <sub>11</sub>	Li*C <sub>17</sub> H <sub>17</sub>
Li*C <sub>9</sub> H <sub>13</sub>	Li*C <sub>17</sub> H <sub>19</sub>
Li*C <sub>9</sub> H <sub>17</sub>	Li*C <sub>17</sub> H <sub>27</sub>
Li*C <sub>9</sub> H <sub>19</sub>	Li*C <sub>17</sub> H <sub>31</sub>
Li*C <sub>9</sub> H <sub>21</sub> Ge	Li*C <sub>18</sub>
Li*C <sub>10</sub> H <sub>6</sub> Br	Li*C <sub>18</sub> F <sub>15</sub> Ge
Li*C <sub>10</sub> H <sub>7</sub>	Li*C <sub>18</sub> H <sub>15</sub> Cd
Li*C <sub>10</sub> H <sub>8</sub>	Li*C <sub>18</sub> H <sub>15</sub> Ge
Li*C <sub>10</sub> H <sub>9</sub>	Li*C <sub>18</sub> H <sub>21</sub>
Li*C <sub>10</sub> H <sub>9</sub> Fe	Li*C <sub>18</sub> H <sub>22</sub> As
Li*C <sub>10</sub> H <sub>11</sub>	Li*C <sub>18</sub> H <sub>29</sub>

$\text{Li}^*\text{C}_{18}\text{H}_{37}$	$\text{LiN}^*\text{C}_{12}\text{H}_{10}\text{Fe}$
$\text{Li}^*\text{C}_{19}\text{H}_{13}$	$\text{LiN}^*\text{C}_{12}\text{H}_{14}$
$\text{Li}^*\text{C}_{19}\text{H}_{15}$	$\text{LiN}^*\text{C}_{12}\text{H}_{14}\text{Fe}$
$\text{Li}^*\text{C}_{19}\text{H}_{17}\text{Ge}$	$\text{LiN}^*\text{C}_{13}\text{H}_{16}$
$\text{Li}^*\text{C}_{20}\text{H}_{12}$	$\text{LiN}^*\text{C}_{13}\text{H}_{16}\text{Fe}$
$\text{Li}^*\text{C}_{20}\text{H}_{19}\text{Ge}$	$\text{LiN}^*\text{C}_{14}\text{H}_{12}$
$\text{Li}^*\text{C}_{20}\text{H}_{21}$	$\text{LiN}^*\text{C}_{14}\text{H}_{13}\text{BrHg}$
$\text{Li}^*\text{C}_{20}\text{H}_{23}$	$\text{LiN}^*\text{C}_{14}\text{H}_{18}\text{Fe}$
$\text{Li}^*\text{C}_{20}\text{H}_{26}$	$\text{LiN}^*\text{C}_{14}\text{H}_{30}$
$\text{Li}^*\text{C}_{21}\text{H}_{17}$	$\text{LiN}^*\text{C}_{16}\text{H}_{12}$
$\text{Li}^*\text{C}_{21}\text{H}_{19}$	$\text{LiN}^*\text{C}_{17}\text{H}_{18}$
$\text{Li}^*\text{C}_{21}\text{H}_{21}\text{Ge}$	$\text{LiN}^*\text{C}_{19}\text{H}_{22}$
$\text{Li}^*\text{C}_{23}\text{H}_{19}$	$\text{LiN}^*\text{C}_{20}\text{H}_{18}$
$\text{Li}^*\text{C}_{25}\text{H}_{21}\text{As}_2$	$\text{LiN}^*\text{C}_{23}\text{H}_{17}$
$\text{Li}^*\text{C}_{26}\text{H}_{20}$	$\text{LiNO}^*\text{C}_3\text{H}_6$
$\text{Li}^*\text{C}_{26}\text{H}_{23}\text{Ge}$	$\text{LiNO}^*\text{C}_4\text{H}_4$
$\text{Li}^*\text{C}_{36}\text{H}_{30}\text{AuGe}_2$	$\text{LiNO}^*\text{C}_4\text{H}_8$
$\text{Li}^*\text{C}_{54}\text{H}_{45}\text{Ge}_4$	$\text{LiNO}^*\text{C}_5\text{H}_{10}$
$\text{Li}^*\text{Cl}$	$\text{LiNO}^*\text{C}_6\text{H}_8$
$\text{LiMnNO}_3^*\text{C}_{11}\text{H}_{11}$	$\text{LiNO}^*\text{C}_7\text{H}_{14}$
$\text{LiMoO}_4\text{S}^*\text{C}_{21}\text{H}_{15}$	$\text{LiNO}^*\text{C}_9\text{H}_{14}$
$\text{LiN}^*\text{C}_2\text{H}_2$	$\text{LiNO}^*\text{C}_{10}\text{H}_{14}$
$\text{LiN}^*\text{C}_3\text{H}_4$	$\text{LiNO}^*\text{C}_{11}\text{H}_{12}$
$\text{LiN}^*\text{C}_3\text{H}_8$	$\text{LiNO}^*\text{C}_{11}\text{H}_{14}$
$\text{LiN}^*\text{C}_4\text{H}_4$	$\text{LiNO}^*\text{C}_{13}\text{H}_{16}$
$\text{LiN}^*\text{C}_4\text{H}_6$	$\text{LiNO}^*\text{C}_{15}\text{H}_{10}$
$\text{LiN}^*\text{C}_5\text{Cl}_4$	$\text{LiNO}^*\text{C}_{18}\text{H}_{28}$
$\text{LiN}^*\text{C}_5\text{H}_3\text{Br}$	$\text{LiNO}^*\text{C}_{19}\text{H}_{30}$
$\text{LiN}^*\text{C}_5\text{H}_4$	$\text{LiNO}^*\text{C}_{20}\text{H}_{32}$
$\text{LiN}^*\text{C}_6\text{H}_6$	$\text{LiNO}^*\text{C}_{21}\text{H}_{22}$
$\text{LiN}^*\text{C}_6\text{H}_{11}\text{Br}$	$\text{LiNOS}^*\text{C}_3\text{H}_8$
$\text{LiN}^*\text{C}_6\text{H}_{12}$	$\text{LiNOS}^*\text{C}_7\text{H}_{12}$
$\text{LiN}^*\text{C}_7\text{H}_3\text{Cl}$	$\text{LiNOS}^*\text{C}_8\text{H}_8$
$\text{LiN}^*\text{C}_7\text{H}_4$	$\text{LiNOS}^*\text{C}_8\text{H}_{10}$
$\text{LiN}^*\text{C}_7\text{H}_{12}$	$\text{LiNOS}_2^*\text{C}_7\text{H}_{12}$
$\text{LiN}^*\text{C}_8\text{H}_5\text{Br}$	$\text{LiNOSi}^*\text{C}_7\text{H}_{14}$
$\text{LiN}^*\text{C}_8\text{H}_6$	$\text{LiNOSi}^*\text{C}_7\text{H}_{16}$
$\text{LiN}^*\text{C}_8\text{H}_8$	$\text{LiNOSi}^*\text{C}_8\text{H}_{14}$
$\text{LiN}^*\text{C}_8\text{H}_9\text{BrHg}$	$\text{LiNOSi}^*\text{C}_{11}\text{H}_{14}$
$\text{LiN}^*\text{C}_8\text{H}_{10}$	$\text{LiNO}_2^*\text{C}_4\text{H}_6$
$\text{LiN}^*\text{C}_8\text{H}_{14}$	$\text{LiNO}_2^*\text{C}_6\text{H}_4$
$\text{LiN}^*\text{C}_9\text{H}_6$	$\text{LiNO}_2^*\text{C}_6\text{H}_5$
$\text{LiN}^*\text{C}_9\text{H}_{10}$	$\text{LiNO}_2^*\text{C}_6\text{H}_{12}$
$\text{LiN}^*\text{C}_9\text{H}_{11}\text{BrHg}$	$\text{LiNO}_2^*\text{C}_7\text{H}_6$
$\text{LiN}^*\text{C}_9\text{H}_{11}\text{Cl}$	$\text{LiNO}_2^*\text{C}_9\text{H}_{12}$
$\text{LiN}^*\text{C}_9\text{H}_{12}$	$\text{LiNO}_2^*\text{C}_9\text{H}_{14}$
$\text{LiN}^*\text{C}_{10}\text{H}_{10}$	$\text{LiNO}_2^*\text{C}_{12}\text{H}_{14}$
$\text{LiN}^*\text{C}_{10}\text{H}_{12}$	$\text{LiNO}_2^*\text{C}_{12}\text{H}_{16}$
$\text{LiN}^*\text{C}_{10}\text{H}_{14}$	$\text{LiNO}_2\text{P}^*\text{C}_{17}\text{H}_{19}$
$\text{LiN}^*\text{C}_{10}\text{H}_{18}$	$\text{LiNO}_2\text{S}^*\text{C}_3\text{H}_8$
$\text{LiN}^*\text{C}_{11}\text{H}_{10}$	$\text{LiNO}_2\text{S}^*\text{C}_5\text{H}_{10}$
$\text{LiN}^*\text{C}_{12}\text{H}_{10}$	$\text{LiNO}_2\text{S}^*\text{C}_8\text{H}_{10}$

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$\text{LiNO}_2\text{S}^*\text{C}_{12}\text{H}_{14}$	$\text{LiN}_2\text{O}^*\text{C}_{11}\text{H}_{19}$
$\text{LiNO}_2\text{S}^*\text{C}_{16}\text{H}_{18}$	$\text{LiN}_2\text{OP}^*\text{C}_5\text{H}_{13}\text{Cl}$
$\text{LiNO}_3^*\text{C}_5\text{H}_{10}$	$\text{LiN}_2\text{OP}^*\text{C}_5\text{H}_{14}$
$\text{LiNO}_3^*\text{C}_{14}\text{H}_{20}$	$\text{LiN}_2\text{OP}^*\text{C}_7\text{H}_{16}$
$\text{LiNO}_3^*\text{C}_{15}\text{H}_{20}$	$\text{LiN}_2\text{OP}^*\text{C}_9\text{H}_{19}$
$\text{LiNO}_3\text{P}^*\text{C}_6\text{H}_{11}$	$\text{LiN}_2\text{O}_2^*\text{C}_4\text{H}_5$
$\text{LiNO}_3\text{P}^*\text{C}_8\text{H}_{15}$	$\text{LiN}_2\text{O}_2\text{P}^*\text{C}_7\text{H}_{16}$
$\text{LiNO}_3\text{P}^*\text{C}_9\text{H}_{19}$	$\text{LiN}_2\text{S}_4^*\text{C}_{11}\text{H}_{21}$
$\text{LiNO}_3\text{S}^*\text{C}_9\text{H}_{10}$	$\text{LiN}_2\text{Si}^*\text{C}_4\text{H}_9$
$\text{LiNO}_3\text{S}_2^*\text{C}_9\text{H}_{12}$	$\text{LiN}_3^*\text{C}_8\text{H}_6$
$\text{LiNO}_3\text{S}_2^*\text{C}_{14}\text{H}_{14}$	$\text{LiN}_3^*\text{C}_{15}\text{H}_{12}$
$\text{LiNP}_2^*\text{C}_6\text{H}_{16}$	$\text{LiN}_3\text{OP}^*\text{C}_6\text{H}_{17}$
$\text{LiNS}^*\text{C}_3\text{HI}$	$\text{LiN}_3\text{OP}^*\text{C}_{12}\text{H}_{19}$
$\text{LiNS}^*\text{C}_3\text{H}_2$	$\text{LiN}_3\text{OP}^*\text{C}_{12}\text{H}_{21}$
$\text{LiNS}^*\text{C}_3\text{H}_6$	$\text{LiN}_4^*\text{C}_2\text{H}_3$
$\text{LiNS}^*\text{C}_5\text{H}_6$	$\text{LiN}_4^*\text{C}_{12}\text{H}_9$
$\text{LiNS}^*\text{C}_5\text{H}_8$	$\text{LiN}_4^*\text{C}_{12}\text{H}_{10}$
$\text{LiNS}^*\text{C}_6\text{H}_{14}$	$\text{LiO}^*\text{C}_2\text{H}_5$
$\text{LiNS}^*\text{C}_7\text{H}_{14}$	$\text{LiO}^*\text{C}_3\text{H}_2\text{K}$
$\text{LiNS}^*\text{C}_8\text{H}_6$	$\text{LiO}^*\text{C}_3\text{H}_5$
$\text{LiNS}^*\text{C}_8\text{H}_8$	$\text{LiO}^*\text{C}_3\text{H}_7$
$\text{LiNS}^*\text{C}_{11}\text{H}_{14}$	$\text{LiO}^*\text{C}_4\text{H}_2\text{Br}$
$\text{LiNSSi}^*\text{C}_7\text{H}_{16}$	$\text{LiO}^*\text{C}_4\text{H}_3$
$\text{LiNS}_2^*\text{C}_4\text{H}_6$	$\text{LiO}^*\text{C}_4\text{H}_4\text{Cl}$
$\text{LiNS}_2^*\text{C}_4\text{H}_8$	$\text{LiO}^*\text{C}_4\text{H}_5$
$\text{LiNS}_2^*\text{C}_5\text{H}_6$	$\text{LiO}^*\text{C}_4\text{H}_6\text{Br}$
$\text{LiNS}_2^*\text{C}_6\text{H}_{10}$	$\text{LiO}^*\text{C}_4\text{H}_6\text{Cl}$
$\text{LiNS}_2^*\text{C}_9\text{H}_{10}$	$\text{LiO}^*\text{C}_4\text{H}_7$
$\text{LiNS}_3^*\text{C}_5\text{H}_{10}$	$\text{LiO}^*\text{C}_4\text{H}_9$
$\text{LiNSE}^*\text{C}_5\text{H}_2$	$\text{LiO}^*\text{C}_5\text{H}_7$
$\text{LiNSE}^*\text{C}_{14}\text{H}_{18}$	$\text{LiO}^*\text{C}_5\text{H}_8\text{Br}$
$\text{LiNSi}^*\text{C}_5\text{H}_{10}$	$\text{LiO}^*\text{C}_5\text{H}_9$
$\text{LiN}_2^*\text{C}_4\text{H}_5$	$\text{LiO}^*\text{C}_5\text{H}_{11}$
$\text{LiN}_2^*\text{C}_5\text{H}_7$	$\text{LiO}^*\text{C}_6\text{H}_9$
$\text{LiN}_2^*\text{C}_5\text{H}_{11}$	$\text{LiO}^*\text{C}_7\text{H}_6\text{F}$
$\text{LiN}_2^*\text{C}_6\text{H}_9$	$\text{LiO}^*\text{C}_8\text{H}_7$
$\text{LiN}_2^*\text{C}_6\text{H}_{11}$	$\text{LiO}^*\text{C}_8\text{H}_{13}$
$\text{LiN}_2^*\text{C}_6\text{H}_{13}$	$\text{LiO}^*\text{C}_8\text{H}_7$
$\text{LiN}_2^*\text{C}_7\text{H}_7$	$\text{LiO}^*\text{C}_8\text{H}_8\text{BrHg}$
$\text{LiN}_2^*\text{C}_7\text{H}_9$	$\text{LiO}^*\text{C}_8\text{H}_9$
$\text{LiN}_2^*\text{C}_7\text{H}_{11}$	$\text{LiO}^*\text{C}_8\text{H}_{13}$
$\text{LiN}_2^*\text{C}_9\text{H}_7$	$\text{LiO}^*\text{C}_9\text{H}_{17}$
$\text{LiN}_2^*\text{C}_{10}\text{H}_8$	$\text{LiO}^*\text{C}_9\text{H}_{15}$
$\text{LiN}_2^*\text{C}_{11}\text{H}_{11}$	$\text{LiO}^*\text{C}_9\text{H}_{17}$
$\text{LiN}_2^*\text{C}_{11}\text{H}_{15}$	$\text{LiO}^*\text{C}_9\text{H}_{19}$
$\text{LiN}_2^*\text{C}_{15}\text{H}_{15}$	$\text{LiO}^*\text{C}_{10}\text{H}_{13}$
$\text{LiN}_2^*\text{C}_{18}\text{H}_{24}\text{Cu}$	$\text{LiO}^*\text{C}_{10}\text{H}_{21}$
$\text{LiN}_2\text{O}^*\text{C}_2\text{H}_5$	$\text{LiO}^*\text{C}_{11}\text{H}_{11}$
$\text{LiN}_2\text{O}^*\text{C}_3\text{H}_3$	$\text{LiO}^*\text{C}_{12}\text{H}_8\text{Cl}$
$\text{LiN}_2\text{O}^*\text{C}_3\text{H}_5$	$\text{LiO}^*\text{C}_{12}\text{H}_9$
$\text{LiN}_2\text{O}^*\text{C}_4\text{H}_7$	$\text{LiO}^*\text{C}_{13}\text{H}_{12}\text{As}$
$\text{LiN}_2\text{O}^*\text{C}_9\text{H}_{19}$	$\text{LiO}^*\text{C}_{14}\text{H}_{14}\text{As}$

LiO*C <sub>19</sub> H <sub>15</sub>	LiOSi*C <sub>7</sub> H <sub>15</sub>
LiO*H	LiOSi*C <sub>7</sub> H <sub>17</sub>
LiOP*C <sub>12</sub> H <sub>14</sub>	LiOSi*C <sub>9</sub> H <sub>19</sub>
LiOP*C <sub>13</sub> H <sub>12</sub>	LiOSi*C <sub>11</sub> H <sub>23</sub>
LiOP*C <sub>14</sub> H <sub>14</sub>	LiOSi*C <sub>12</sub> H <sub>21</sub>
LiOP*C <sub>15</sub> H <sub>16</sub>	LiOSi*C <sub>12</sub> H <sub>25</sub>
LiOP*C <sub>16</sub> H <sub>16</sub>	LiOSi*C <sub>20</sub> H <sub>17</sub>
LiOP*C <sub>23</sub> H <sub>20</sub> Fe	LiO <sub>2</sub> *C <sub>4</sub> H <sub>5</sub> Cl <sub>2</sub>
LiOPS*C <sub>8</sub> H <sub>14</sub>	LiO <sub>2</sub> *C <sub>4</sub> H <sub>7</sub>
LiOPS*C <sub>19</sub> H <sub>16</sub>	LiO <sub>2</sub> *C <sub>5</sub> H <sub>9</sub>
LiOS*C <sub>2</sub> H <sub>5</sub>	LiO <sub>2</sub> *C <sub>5</sub> H <sub>11</sub>
LiOS*C <sub>4</sub> H <sub>7</sub>	LiO <sub>2</sub> *C <sub>6</sub> H <sub>8</sub> Cl
LiOS*C <sub>5</sub> H <sub>7</sub>	LiO <sub>2</sub> *C <sub>6</sub> H <sub>11</sub>
LiOS*C <sub>5</sub> H <sub>9</sub>	LiO <sub>2</sub> *C <sub>6</sub> H <sub>13</sub>
LiOS*C <sub>5</sub> H <sub>11</sub>	LiO <sub>2</sub> *C <sub>7</sub> H <sub>11</sub>
LiOS*C <sub>7</sub> H <sub>6</sub> Cl	LiO <sub>2</sub> *C <sub>7</sub> H <sub>15</sub>
LiOS*C <sub>7</sub> H <sub>7</sub>	LiO <sub>2</sub> *C <sub>8</sub> H <sub>9</sub>
LiOS*C <sub>7</sub> H <sub>9</sub>	LiO <sub>2</sub> *C <sub>8</sub> H <sub>11</sub>
LiOS*C <sub>7</sub> H <sub>15</sub>	LiO <sub>2</sub> *C <sub>8</sub> H <sub>13</sub>
LiOS*C <sub>7</sub> H <sub>15</sub> Ge	LiO <sub>2</sub> *C <sub>9</sub> H <sub>9</sub>
LiOS*C <sub>8</sub> H <sub>9</sub>	LiO <sub>2</sub> *C <sub>9</sub> H <sub>11</sub>
LiOS*C <sub>9</sub> H <sub>9</sub>	LiO <sub>2</sub> *C <sub>9</sub> H <sub>17</sub>
LiOS*C <sub>9</sub> H <sub>17</sub>	LiO <sub>2</sub> *C <sub>10</sub> H <sub>12</sub> Br
LiOS*C <sub>10</sub> H <sub>11</sub>	LiO <sub>2</sub> *C <sub>10</sub> H <sub>21</sub>
LiOS*C <sub>14</sub> H <sub>19</sub>	LiO <sub>2</sub> *C <sub>11</sub> H <sub>11</sub>
LiOS*C <sub>18</sub> H <sub>27</sub>	LiO <sub>2</sub> *C <sub>11</sub> H <sub>13</sub>
LiOS*C <sub>21</sub> H <sub>17</sub>	LiO <sub>2</sub> *C <sub>11</sub> H <sub>15</sub>
LiOSSI*C <sub>7</sub> H <sub>15</sub>	LiO <sub>2</sub> *C <sub>11</sub> H <sub>21</sub>
LiOSSI*C <sub>10</sub> H <sub>15</sub>	LiO <sub>2</sub> *C <sub>11</sub> H <sub>23</sub>
LiO <sub>2</sub> *C <sub>3</sub> H <sub>7</sub>	LiO <sub>2</sub> *C <sub>12</sub> H <sub>15</sub>
LiO <sub>2</sub> *C <sub>4</sub> H <sub>7</sub>	LiO <sub>2</sub> *C <sub>12</sub> H <sub>17</sub>
LiO <sub>2</sub> *C <sub>4</sub> H <sub>9</sub>	LiO <sub>2</sub> *C <sub>17</sub> H <sub>25</sub>
LiO <sub>2</sub> *C <sub>6</sub> H <sub>11</sub>	LiO <sub>2</sub> *C <sub>18</sub> H <sub>27</sub>
LiO <sub>2</sub> *C <sub>8</sub> H <sub>15</sub>	LiO <sub>2</sub> P*C <sub>8</sub> H <sub>14</sub>
LiO <sub>2</sub> *C <sub>9</sub> H <sub>15</sub>	LiO <sub>2</sub> PS*C <sub>3</sub> H <sub>8</sub>
LiO <sub>2</sub> *C <sub>12</sub> H <sub>13</sub>	LiO <sub>2</sub> PS*C <sub>5</sub> H <sub>11</sub> Cl
LiO <sub>2</sub> *C <sub>13</sub> H <sub>15</sub>	LiO <sub>2</sub> P <sub>2</sub> *C <sub>25</sub> H <sub>21</sub>
LiOSe*C <sub>7</sub> H <sub>7</sub>	LiO <sub>2</sub> S*C <sub>2</sub> H <sub>5</sub>
LiOSe*C <sub>8</sub> H <sub>9</sub>	LiO <sub>2</sub> S*C <sub>6</sub> H <sub>9</sub>
LiOSe*C <sub>9</sub> H <sub>8</sub> F <sub>3</sub>	LiO <sub>2</sub> S*C <sub>6</sub> H <sub>11</sub>
LiOSe*C <sub>9</sub> H <sub>11</sub>	LiO <sub>2</sub> S*C <sub>7</sub> H <sub>7</sub>
LiOSe*C <sub>11</sub> H <sub>11</sub>	LiO <sub>2</sub> S*C <sub>9</sub> H <sub>9</sub>
LiOSe*C <sub>13</sub> H <sub>11</sub>	LiO <sub>2</sub> S*C <sub>10</sub> H <sub>11</sub>
LiOSe*C <sub>14</sub> H <sub>11</sub>	LiO <sub>2</sub> S*C <sub>11</sub> H <sub>13</sub>
LiOSe*C <sub>14</sub> H <sub>13</sub>	LiO <sub>2</sub> S*C <sub>11</sub> H <sub>19</sub>
LiOSe*C <sub>14</sub> H <sub>17</sub>	LiO <sub>2</sub> S*C <sub>12</sub> H <sub>8</sub> Br
LiOSe*C <sub>15</sub> H <sub>15</sub>	LiO <sub>2</sub> S*C <sub>12</sub> H <sub>9</sub>
LiOSe*C <sub>17</sub> H <sub>27</sub>	LiO <sub>2</sub> S*C <sub>21</sub> H <sub>17</sub>
LiOSi*C <sub>4</sub> H <sub>11</sub>	LiO <sub>2</sub> Se*C <sub>9</sub> H <sub>9</sub>
LiOSi*C <sub>5</sub> H <sub>11</sub>	LiO <sub>2</sub> Se*C <sub>9</sub> H <sub>13</sub>
LiOSi*C <sub>5</sub> H <sub>13</sub>	LiO <sub>2</sub> Se*C <sub>11</sub> H <sub>11</sub>
LiOSi*C <sub>6</sub> H <sub>13</sub>	LiO <sub>2</sub> Si*C <sub>7</sub> H <sub>15</sub>



- $\text{LiO}_2\text{Si}^*\text{C}_9\text{H}_{18}\text{Cl}$   
 $\text{LiO}_2\text{Si}^*\text{C}_9\text{H}_{19}$   
 $\text{LiO}_2\text{Si}^*\text{C}_{10}\text{H}_{22}\text{B}$   
 $\text{LiO}_2\text{Si}_2^*\text{C}_{12}\text{H}_{27}$   
 $\text{LiO}_3^*\text{C}_9\text{H}_5\text{Cr}$   
 $\text{LiO}_3^*\text{C}_9\text{H}_9$   
 $\text{LiO}_3^*\text{C}_9\text{H}_{13}$   
 $\text{LiO}_3^*\text{C}_9\text{H}_{15}$   
 $\text{LiO}_3^*\text{C}_{12}\text{H}_{17}$   
 $\text{LiO}_3\text{P}^*\text{C}_3\text{H}_8$   
 $\text{LiO}_3\text{P}^*\text{C}_5\text{H}_{10}\text{Cl}_2$   
 $\text{LiO}_3\text{P}^*\text{C}_5\text{H}_{11}\text{Cl}$   
 $\text{LiO}_3\text{P}^*\text{C}_8\text{H}_{16}$   
 $\text{LiO}_3\text{PS}^*\text{C}_6\text{H}_{14}$   
 $\text{LiO}_3\text{Re}^*\text{C}_8\text{H}_4$   
 $\text{LiO}_3\text{S}^*\text{C}_2\text{H}_5$   
 $\text{LiO}_3\text{S}^*\text{C}_4\text{H}_7$   
 $\text{LiO}_3\text{S}^*\text{C}_5\text{H}_9$   
 $\text{LiO}_3\text{S}^*\text{C}_8\text{H}_7$   
 $\text{LiO}_3\text{S}^*\text{C}_8\text{H}_9$   
 $\text{LiO}_3\text{S}^*\text{C}_{15}\text{H}_{13}$   
 $\text{LiO}_3\text{Si}_4^*\text{C}_{21}\text{H}_{31}$   
 $\text{LiO}_4^*\text{C}_5\text{H}_9$   
 $\text{LiO}_4^*\text{C}_7\text{H}_{13}\text{B}_2$   
 $\text{LiO}_4^*\text{C}_{10}\text{H}_{15}$   
 $\text{LiO}_4\text{P}^*\text{C}_6\text{H}_{12}$   
 $\text{LiO}_4\text{P}^*\text{C}_7\text{H}_{14}$   
 $\text{LiO}_4\text{P}^*\text{C}_{26}\text{H}_{26}$   
 $\text{LiO}_4\text{S}^*\text{C}_{21}\text{H}_{15}\text{Cr}$   
 $\text{LiO}_4\text{SW}^*\text{C}_{21}\text{H}_{15}$   
 $\text{LiO}_4\text{Si}^*\text{C}_{18}\text{H}_{25}\text{Cr}$   
 $\text{LiO}_4\text{Si}_2^*\text{C}_9\text{H}_{19}$   
 $\text{LiO}_5^*\text{C}_8\text{H}_{11}$   
 $\text{LiO}_5\text{P}^*\text{C}_7\text{H}_{14}$   
 $\text{LiO}_5\text{P}^*\text{C}_8\text{H}_{18}$   
 $\text{LiO}_5\text{P}^*\text{C}_{10}\text{H}_{20}$   
 $\text{LiO}_5\text{PS}^*\text{C}_6\text{H}_{14}$   
 $\text{LiO}_5\text{SSI}^*\text{C}_{24}\text{H}_{35}$   
 $\text{LiO}_6^*\text{C}_{10}\text{H}_{18}\text{B}_3$   
 $\text{LiO}_6\text{P}_2^*\text{C}_9\text{H}_{20}\text{Cl}$   
 $\text{LiO}_6\text{Si}_3^*\text{C}_{21}\text{H}_{57}\text{Hg}$   
 $\text{LiP}^*\text{C}_3\text{H}_8$   
 $\text{LiP}^*\text{C}_8\text{H}_{18}$   
 $\text{LiP}^*\text{C}_9\text{H}_{20}$   
 $\text{LiP}^*\text{C}_{12}\text{H}_{10}$   
 $\text{LiP}^*\text{C}_{13}\text{H}_{12}$   
 $\text{LiP}^*\text{C}_{18}\text{H}_{22}$   
 $\text{LiP}^*\text{C}_{19}\text{H}_{16}$   
 $\text{LiPS}^*\text{C}_8\text{H}_{10}$   
 $\text{LiPS}^*\text{C}_{12}\text{H}_{14}$   
 $\text{LiPS}^*\text{C}_{13}\text{H}_{18}$   
 $\text{LiPS}^*\text{C}_{23}\text{H}_{20}\text{Fe}$   
 $\text{LiPSi}_2^*\text{C}_{19}\text{H}_{28}$   
 $\text{LiP}_2^*\text{C}_5\text{H}_{13}$   
 $\text{LiP}_2^*\text{C}_6\text{H}_{18}\text{B}$   
 $\text{LiP}_2^*\text{C}_{25}\text{H}_{21}$   
 $\text{LiP}_3^*\text{C}_7\text{H}_{18}$   
**LiPb**  
     LiPb  
         Formation: 5.5.7.1.1  
 $\text{LiPb}^*\text{C}_3\text{H}_9$   
 $\text{LiPb}^*\text{C}_6\text{H}_{15}$   
 $\text{LiPb}^*\text{C}_{18}\text{F}_{15}$   
 $\text{LiPb}^*\text{C}_{18}\text{H}_{15}$   
 $\text{LiPb}^*\text{C}_{19}\text{H}_{15}\text{Cl}_2$   
 $\text{LiPb}^*\text{C}_{19}\text{H}_{17}$   
 $\text{LiPb}^*\text{C}_{21}\text{H}_{21}$   
 $\text{LiPb}^*\text{C}_{31}\text{H}_{26}\text{As}$   
 $\text{LiPb}^*\text{C}_{33}\text{H}_{31}\text{Ge}$   
 $\text{LiPbSi}^*\text{C}_{22}\text{H}_{25}$   
 $\text{LiPb}_2^*\text{C}_{37}\text{H}_{31}$   
 $\text{LiS}^*\text{C}_2\text{H}_5$   
 $\text{LiS}^*\text{C}_4\text{Cl}_3$   
 $\text{LiS}^*\text{C}_4\text{H}_2\text{Br}$   
 $\text{LiS}^*\text{C}_4\text{H}_2\text{Cl}$   
 $\text{LiS}^*\text{C}_4\text{H}_2\text{F}$   
 $\text{LiS}^*\text{C}_4\text{H}_2\text{I}$   
 $\text{LiS}^*\text{C}_4\text{H}_3$   
 $\text{LiS}^*\text{C}_4\text{H}_7$   
 $\text{LiS}^*\text{C}_5\text{H}_7$   
 $\text{LiS}^*\text{C}_6\text{H}_5$   
 $\text{LiS}^*\text{C}_6\text{H}_9$   
 $\text{LiS}^*\text{C}_6\text{H}_9\text{ClF}$   
 $\text{LiS}^*\text{C}_7\text{H}_7$   
 $\text{LiS}^*\text{C}_8\text{H}_7$   
 $\text{LiS}^*\text{C}_8\text{H}_9$   
 $\text{LiS}^*\text{C}_8\text{H}_{13}$   
 $\text{LiS}^*\text{C}_9\text{H}_9$   
 $\text{LiS}^*\text{C}_9\text{H}_9\text{F}_3$   
 $\text{LiS}^*\text{C}_9\text{H}_{11}$   
 $\text{LiS}^*\text{C}_{10}\text{H}_{11}$   
 $\text{LiS}^*\text{C}_{10}\text{H}_{13}$   
 $\text{LiS}^*\text{C}_{11}\text{H}_{11}$   
 $\text{LiS}^*\text{C}_{11}\text{H}_{13}$   
 $\text{LiS}^*\text{C}_{11}\text{H}_{15}$   
 $\text{LiS}^*\text{C}_{12}\text{H}_{17}$   
 $\text{LiS}^*\text{C}_{13}\text{H}_{11}$   
 $\text{LiS}^*\text{C}_{13}\text{H}_{15}$   
 $\text{LiS}^*\text{C}_{14}\text{H}_{11}$   
 $\text{LiS}^*\text{C}_{14}\text{H}_{13}$   
 $\text{LiS}^*\text{C}_{14}\text{H}_{17}$   
 $\text{LiS}^*\text{C}_{20}\text{H}_{15}$   
 $\text{LiS}^*\text{C}_{21}\text{H}_{17}$   
 $\text{LiSSI}^*\text{C}_{10}\text{H}_{15}$

$\text{LiSSi}^*\text{C}_{15}\text{H}_{25}$   
 $\text{LiSSi}^*\text{C}_{16}\text{H}_{20}$   
 $\text{LiS}_2^*\text{C}_3\text{H}_7$   
 $\text{LiS}_2^*\text{C}_4\text{H}_3$   
 $\text{LiS}_2^*\text{C}_4\text{H}_7$   
 $\text{LiS}_2^*\text{C}_5\text{H}_5$   
 $\text{LiS}_2^*\text{C}_5\text{H}_9$   
 $\text{LiS}_2^*\text{C}_6\text{H}_9$   
 $\text{LiS}_2^*\text{C}_6\text{H}_{11}$   
 $\text{LiS}_2^*\text{C}_7\text{H}_5$   
 $\text{LiS}_2^*\text{C}_9\text{H}_{13}$   
 $\text{LiS}_2^*\text{C}_9\text{H}_{15}$   
 $\text{LiS}_2^*\text{C}_9\text{H}_{17}$   
 $\text{LiS}_2^*\text{C}_{13}\text{H}_{11}$   
 $\text{LiS}_2^*\text{C}_{14}\text{H}_{13}$   
 $\text{LiS}_2^*\text{C}_{16}\text{H}_{23}$   
 $\text{LiS}_2\text{Si}^*\text{C}_7\text{H}_{15}$   
 $\text{LiS}_2\text{Sn}^*\text{C}_6\text{H}_{15}$   
 $\text{LiS}_3^*\text{C}_3\text{H}_5$   
 $\text{LiS}_3^*\text{C}_5\text{H}_9$   
 $\text{LiS}_3^*\text{C}_{19}\text{H}_{15}$   
 $\text{LiS}_3^*\text{C}_{55}\text{H}_{45}$   
 $\text{LiS}_4^*\text{C}_4\text{H}_7$   
 $\text{LiS}_4^*\text{C}_6\text{H}_3$   
 $\text{LiSb}^*\text{C}_{12}\text{H}_{10}$   
 $\text{LiSb}^*\text{C}_{13}\text{H}_{12}$   
 $\text{LiSb}_2^*\text{C}_{25}\text{H}_{21}$   
 $\text{LiSe}^*\text{C}_4\text{H}_3$   
 $\text{LiSe}^*\text{C}_6\text{H}_5$   
 $\text{LiSe}^*\text{C}_7\text{H}_7$   
 $\text{LiSe}^*\text{C}_8\text{H}_6\text{F}_3$   
 $\text{LiSe}^*\text{C}_8\text{H}_7$   
 $\text{LiSe}^*\text{C}_9\text{H}_6\text{F}_3$   
 $\text{LiSe}^*\text{C}_9\text{H}_9$   
 $\text{LiSe}^*\text{C}_{10}\text{H}_8\text{F}_3$   
 $\text{LiSe}^*\text{C}_{10}\text{H}_{11}$   
 $\text{LiSe}^*\text{C}_{11}\text{H}_{15}$   
 $\text{LiSe}^*\text{C}_{12}\text{H}_{17}$   
 $\text{LiSe}^*\text{C}_{13}\text{H}_{11}$   
 $\text{LiSe}^*\text{C}_{14}\text{H}_{11}$   
 $\text{LiSe}^*\text{C}_{14}\text{H}_{13}$   
 $\text{LiSeSi}^*\text{C}_{10}\text{H}_{15}$   
 $\text{LiSeSi}^*\text{C}_{11}\text{H}_{14}\text{F}_3$   
 $\text{LiSe}_2^*\text{C}_{13}\text{H}_{11}$   
 $\text{LiSe}_2^*\text{C}_{14}\text{H}_{13}$   
 $\text{LiSe}_2^*\text{C}_{19}\text{H}_{23}$   
 $\text{LiSe}_3^*\text{C}_{19}\text{H}_{15}$   
 $\text{LiSi}^*\text{C}_3\text{H}_9$   
 $\text{LiSi}^*\text{C}_4\text{H}_9\text{Br}_2$   
 $\text{LiSi}^*\text{C}_4\text{H}_9\text{Cl}_2$   
 $\text{LiSi}^*\text{C}_4\text{H}_{10}\text{Cl}$   
 $\text{LiSi}^*\text{C}_4\text{H}_{11}$

$\text{LiSi}^*\text{C}_5\text{H}_{11}$   
 $\text{LiSi}^*\text{C}_5\text{H}_{13}$   
 $\text{LiSi}^*\text{C}_6\text{H}_{11}$   
 $\text{LiSi}^*\text{C}_6\text{H}_{11}\text{Cl}_2$   
 $\text{LiSi}^*\text{C}_6\text{H}_{12}\text{Cl}$   
 $\text{LiSi}^*\text{C}_6\text{H}_{13}$   
 $\text{LiSi}^*\text{C}_6\text{H}_{15}$   
 $\text{LiSi}^*\text{C}_8\text{H}_{11}$   
 $\text{LiSi}^*\text{C}_8\text{H}_{15}$   
 $\text{LiSi}^*\text{C}_8\text{H}_{18}\text{Cl}$   
 $\text{LiSi}^*\text{C}_8\text{H}_{19}$   
 $\text{LiSi}^*\text{C}_9\text{H}_{11}\text{ClF}$   
 $\text{LiSi}^*\text{C}_9\text{H}_{19}$   
 $\text{LiSi}^*\text{C}_9\text{H}_{21}$   
 $\text{LiSi}^*\text{C}_{10}\text{H}_{15}$   
 $\text{LiSi}^*\text{C}_{12}\text{H}_{11}$   
 $\text{LiSi}^*\text{C}_{12}\text{H}_{19}$   
 $\text{LiSi}^*\text{C}_{12}\text{H}_{27}$   
 $\text{LiSi}^*\text{C}_{13}\text{H}_{13}$   
 $\text{LiSi}^*\text{C}_{16}\text{H}_{19}$   
 $\text{LiSi}^*\text{C}_{17}\text{H}_{17}$   
 $\text{LiSi}^*\text{C}_{18}\text{H}_{15}$   
 $\text{LiSi}^*\text{C}_{20}\text{H}_{19}$   
 $\text{LiSi}^*\text{C}_{21}\text{H}_{27}$   
 $\text{LiSi}^*\text{C}_{26}\text{H}_{23}$   
 $\text{LiSi}^*\text{C}_{54}\text{H}_{45}\text{Ge}_3$   
 $\text{LiSi}_2^*\text{CCl}_7$   
 $\text{LiSi}_2^*\text{C}_7\text{H}_{18}\text{Br}$   
 $\text{LiSi}_2^*\text{C}_7\text{H}_{19}$   
 $\text{LiSi}_2^*\text{C}_{12}\text{H}_{29}$   
 $\text{LiSi}_2^*\text{C}_{18}\text{H}_{33}$   
 $\text{LiSi}_2^*\text{C}_{25}\text{H}_{23}$   
 $\text{LiSi}_2^*\text{C}_{30}\text{H}_{25}$   
 $\text{LiSi}_3^*\text{C}_{10}\text{H}_{27}$   
 $\text{LiSi}_3^*\text{C}_{12}\text{H}_{23}$   
 $\text{LiSi}_3^*\text{C}_{12}\text{H}_{33}\text{Ge}$   
 $\text{LiSi}_3\text{Sn}^*\text{C}_{12}\text{H}_{33}$   
 $\text{LiSi}_4^*\text{C}_6\text{H}_{21}$   
 $\text{LiSi}_4^*\text{C}_9\text{H}_{27}$   
 $\text{LiSi}_4^*\text{C}_{13}\text{H}_{35}$   
 $\text{LiSi}_4^*\text{C}_{49}\text{H}_{43}$   
**LiSn**

LiSn

Formation: 5.5.6.1.1

$\text{LiSn}^*\text{C}_3\text{H}_9$   
 $\text{LiSn}^*\text{C}_4\text{H}_9\text{BrCl}$   
 $\text{LiSn}^*\text{C}_4\text{H}_9\text{Br}_2$   
 $\text{LiSn}^*\text{C}_4\text{H}_9\text{Cl}_2$   
 $\text{LiSn}^*\text{C}_6\text{H}_{15}$   
 $\text{LiSn}^*\text{C}_8\text{H}_{15}$   
 $\text{LiSn}^*\text{C}_9\text{H}_{21}$   
 $\text{LiSn}^*\text{C}_{11}\text{H}_{17}$

$\text{LiSn}^*\text{C}_{12}\text{H}_{27}$   
 $\text{LiSn}^*\text{C}_{13}\text{H}_{13}$   
 $\text{LiSn}^*\text{C}_{13}\text{H}_{23}$   
 $\text{LiSn}^*\text{C}_{14}\text{H}_{27}$   
 $\text{LiSn}^*\text{C}_{14}\text{H}_{29}$   
 $\text{LiSn}^*\text{C}_{16}\text{H}_{19}$   
 $\text{LiSn}^*\text{C}_{18}\text{H}_{15}$   
 $\text{LiSn}^*\text{C}_{19}\text{H}_{17}$   
 $\text{LiSn}^*\text{C}_{20}\text{H}_{17}$   
 $\text{LiSn}^*\text{C}_{21}\text{H}_{21}$   
 $\text{LiSn}^*\text{C}_{31}\text{H}_{26}\text{As}$   
 $\text{LiSn}^*\text{C}_{39}\text{H}_{30}\text{Co}$   
**LiSn<sub>2</sub>**

LiSn<sub>2</sub>

Formation: 5.5.6.1.1

$\text{LiSn}_2^*\text{C}_5\text{H}_{15}$   
 $\text{LiSn}_2^*\text{C}_{15}\text{H}_{35}$   
 $\text{LiSn}_2^*\text{C}_{37}\text{H}_{31}$   
 $\text{LiSn}_4^*\text{C}_9\text{H}_{27}$   
 $\text{LiSn}_4^*\text{C}_{54}\text{H}_{45}$   
 $\text{LiTe}^*\text{C}_7\text{H}_7$   
 $\text{LiTe}_2^*\text{C}_{13}\text{H}_{11}$   
 $\text{LiZn}^*\text{C}_{18}\text{H}_{15}$   
 $\text{Li}_2^*\text{CH}_2$   
 $\text{Li}_2^*\text{CH}_3\text{Br}$   
 $\text{Li}_2^*\text{C}_2$   
 $\text{Li}_2^*\text{C}_2\text{H}_4$   
 $\text{Li}_2^*\text{C}_3\text{H}_2$   
 $\text{Li}_2^*\text{C}_4\text{H}_6$   
 $\text{Li}_2^*\text{C}_4\text{H}_8$   
 $\text{Li}_2^*\text{C}_5\text{H}_6$   
 $\text{Li}_2^*\text{C}_5\text{H}_{10}$   
 $\text{Li}_2^*\text{C}_6\text{Cl}_4$   
 $\text{Li}_2^*\text{C}_6\text{H}_4$   
 $\text{Li}_2^*\text{C}_6\text{H}_{12}$   
 $\text{Li}_2^*\text{C}_7\text{H}_6$   
 $\text{Li}_2^*\text{C}_7\text{H}_{10}$   
 $\text{Li}_2^*\text{C}_8\text{H}_8$   
 $\text{Li}_2^*\text{C}_9\text{H}_6$   
 $\text{Li}_2^*\text{C}_9\text{H}_8$   
 $\text{Li}_2^*\text{C}_{10}\text{H}_6$   
 $\text{Li}_2^*\text{C}_{10}\text{H}_8$   
 $\text{Li}_2^*\text{C}_{10}\text{H}_{10}$   
 $\text{Li}_2^*\text{C}_{10}\text{H}_{12}$   
 $\text{Li}_2^*\text{C}_{10}\text{H}_{20}$   
 $\text{Li}_2^*\text{C}_{12}\text{H}_6$   
 $\text{Li}_2^*\text{C}_{12}\text{H}_8$   
 $\text{Li}_2^*\text{C}_{12}\text{H}_{10}$   
 $\text{Li}_2^*\text{C}_{12}\text{H}_{10}\text{Ge}$   
 $\text{Li}_2^*\text{C}_{12}\text{H}_{20}$   
 $\text{Li}_2^*\text{C}_{14}\text{H}_{10}$   
 $\text{Li}_2^*\text{C}_{14}\text{H}_{12}$

$\text{Li}_2^*\text{C}_{14}\text{H}_{14}\text{Ge}$   
 $\text{Li}_2^*\text{C}_{15}\text{H}_{14}$   
 $\text{Li}_2^*\text{C}_{16}\text{H}_{10}$   
 $\text{Li}_2^*\text{C}_{16}\text{H}_{12}$   
 $\text{Li}_2^*\text{C}_{16}\text{H}_{14}$   
 $\text{Li}_2^*\text{C}_{16}\text{H}_{16}$   
 $\text{Li}_2^*\text{C}_{18}\text{H}_{12}$   
 $\text{Li}_2^*\text{C}_{18}\text{H}_{14}$   
 $\text{Li}_2^*\text{C}_{18}\text{H}_{16}$   
 $\text{Li}_2^*\text{C}_{18}\text{H}_{18}$   
 $\text{Li}_2^*\text{C}_{18}\text{H}_{20}$   
 $\text{Li}_2^*\text{C}_{20}\text{H}_{12}$   
 $\text{Li}_2^*\text{C}_{22}\text{H}_{14}$   
 $\text{Li}_2^*\text{C}_{24}\text{H}_{20}\text{Ge}_2$   
 $\text{Li}_2^*\text{C}_{26}\text{H}_{18}$   
 $\text{Li}_2^*\text{C}_{26}\text{H}_{20}$   
 $\text{Li}_2^*\text{C}_{28}\text{H}_{20}$   
 $\text{Li}_2^*\text{C}_{28}\text{H}_{22}$   
 $\text{Li}_2^*\text{C}_{28}\text{H}_{24}$   
 $\text{Li}_2^*\text{C}_{30}\text{H}_{36}$   
 $\text{Li}_2\text{N}^*\text{C}_2\text{H}$   
 $\text{Li}_2\text{N}^*\text{C}_5\text{H}_3$   
 $\text{Li}_2\text{N}^*\text{C}_5\text{H}_5$   
 $\text{Li}_2\text{N}^*\text{C}_7\text{H}_{13}$   
 $\text{Li}_2\text{N}^*\text{C}_8\text{H}_9$   
 $\text{Li}_2\text{N}^*\text{C}_9\text{H}_{11}$   
 $\text{Li}_2\text{N}^*\text{C}_{10}\text{H}_7$   
 $\text{Li}_2\text{N}^*\text{C}_{11}\text{H}_{13}$   
 $\text{Li}_2\text{N}^*\text{C}_{12}\text{H}_{13}\text{Fe}$   
 $\text{Li}_2\text{N}^*\text{C}_{14}\text{H}_{13}$   
 $\text{Li}_2\text{N}^*\text{C}_{19}\text{H}_{15}$   
 $\text{Li}_2\text{N}^*\text{C}_{23}\text{H}_{17}$   
 $\text{Li}_2\text{NO}^*\text{C}_3\text{H}_5$   
 $\text{Li}_2\text{NO}^*\text{C}_4\text{H}_9$   
 $\text{Li}_2\text{NO}^*\text{C}_8\text{H}_7$   
 $\text{Li}_2\text{NO}^*\text{C}_8\text{H}_{13}$   
 $\text{Li}_2\text{NO}^*\text{C}_9\text{H}_7$   
 $\text{Li}_2\text{NO}^*\text{C}_9\text{H}_9$   
 $\text{Li}_2\text{NO}^*\text{C}_{10}\text{H}_{12}\text{Cl}$   
 $\text{Li}_2\text{NO}^*\text{C}_{10}\text{H}_{13}$   
 $\text{Li}_2\text{NO}^*\text{C}_{11}\text{H}_{13}$   
 $\text{Li}_2\text{NO}^*\text{C}_{12}\text{H}_{15}$   
 $\text{Li}_2\text{NO}^*\text{C}_{14}\text{H}_{11}$   
 $\text{Li}_2\text{NOS}^*\text{C}_8\text{H}_9$   
 $\text{Li}_2\text{NO}_2^*\text{C}_2\text{H}_4$   
 $\text{Li}_2\text{NO}_2^*\text{C}_3\text{H}_4$   
 $\text{Li}_2\text{NO}_2^*\text{C}_{11}\text{H}_{13}$   
 $\text{Li}_2\text{NO}_2\text{S}^*\text{C}_3\text{H}_7$   
 $\text{Li}_2\text{NO}_2\text{S}^*\text{C}_9\text{H}_7$   
 $\text{Li}_2\text{NS}^*\text{C}_8\text{H}_7$   
 $\text{Li}_2\text{NS}^*\text{C}_9\text{H}_9$   
 $\text{Li}_2\text{N}_2^*\text{C}_9\text{H}_8$

$\text{Li}_2\text{N}_2\text{O}_2\text{S}^*\text{C}_{11}\text{H}_{13}$   
 $\text{Li}_2\text{N}_4^*\text{Au}_2\text{C}_{36}\text{H}_{40}$   
 $\text{Li}_2\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Ag}_2$   
 $\text{Li}_2\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Au}_2$   
 $\text{Li}_2\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Cu}_2$   
 $\text{Li}_2\text{O}^*\text{C}_3\text{H}_4$   
 $\text{Li}_2\text{O}^*\text{C}_3\text{H}_6$   
 $\text{Li}_2\text{O}^*\text{C}_5\text{H}_{10}$   
 $\text{Li}_2\text{O}^*\text{C}_6\text{H}_4$   
 $\text{Li}_2\text{O}^*\text{C}_6\text{H}_{12}$   
 $\text{Li}_2\text{O}^*\text{C}_7\text{H}_6$   
 $\text{Li}_2\text{O}^*\text{C}_7\text{H}_{14}$   
 $\text{Li}_2\text{O}^*\text{C}_8\text{H}_8$   
 $\text{Li}_2\text{O}^*\text{C}_8\text{H}_{16}$   
 $\text{Li}_2\text{O}^*\text{C}_9\text{H}_4\text{F}_6$   
 $\text{Li}_2\text{O}^*\text{C}_9\text{H}_{10}$   
 $\text{Li}_2\text{O}^*\text{C}_9\text{H}_{16}$   
 $\text{Li}_2\text{O}^*\text{C}_9\text{H}_{18}$   
 $\text{Li}_2\text{O}^*\text{C}_{10}\text{H}_8$   
 $\text{Li}_2\text{O}^*\text{C}_{10}\text{H}_{12}$   
 $\text{Li}_2\text{O}^*\text{C}_{11}\text{H}_{14}$   
 $\text{Li}_2\text{O}^*\text{C}_{12}\text{H}_8$   
 $\text{Li}_2\text{O}^*\text{C}_{12}\text{H}_{12}$   
 $\text{Li}_2\text{O}^*\text{C}_{13}\text{H}_{10}$   
 $\text{Li}_2\text{O}^*\text{C}_{13}\text{H}_{16}$   
 $\text{Li}_2\text{O}^*\text{C}_{13}\text{H}_{18}$   
 $\text{Li}_2\text{O}^*\text{C}_{15}\text{H}_{14}$   
 $\text{Li}_2\text{O}^*\text{C}_{20}\text{H}_{14}$   
 $\text{Li}_2\text{O}^*\text{C}_{20}\text{H}_{16}$   
 $\text{Li}_2\text{OS}^*\text{C}_2\text{H}_2$   
 $\text{Li}_2\text{OSn}^*\text{C}_{17}\text{H}_{38}$   
 $\text{Li}_2\text{O}_2^*\text{C}_2\text{Cl}_2$   
 $\text{Li}_2\text{O}_2^*\text{C}_3$   
 $\text{Li}_2\text{O}_2^*\text{C}_3\text{H}_4$   
 $\text{Li}_2\text{O}_2^*\text{C}_4\text{H}_2$   
 $\text{Li}_2\text{O}_2^*\text{C}_4\text{H}_4$   
 $\text{Li}_2\text{O}_2^*\text{C}_4\text{H}_6$   
 $\text{Li}_2\text{O}_2^*\text{C}_5\text{H}_6$   
 $\text{Li}_2\text{O}_2^*\text{C}_6\text{H}_{10}$   
 $\text{Li}_2\text{O}_2^*\text{C}_7\text{H}_4$   
 $\text{Li}_2\text{O}_2^*\text{C}_8\text{H}_6$   
 $\text{Li}_2\text{O}_2^*\text{C}_8\text{H}_{12}$   
 $\text{Li}_2\text{O}_2^*\text{C}_9\text{H}_6$   
 $\text{Li}_2\text{O}_2^*\text{C}_9\text{H}_8$   
 $\text{Li}_2\text{O}_2^*\text{C}_{15}\text{H}_{10}$   
 $\text{Li}_2\text{O}_2^*\text{C}_{16}\text{H}_{12}$   
 $\text{Li}_2\text{O}_2\text{S}^*\text{C}_7\text{H}_6$   
 $\text{Li}_2\text{O}_2\text{S}^*\text{C}_8\text{H}_6$   
 $\text{Li}_2\text{O}_2\text{S}^*\text{C}_8\text{H}_{16}$   
 $\text{Li}_2\text{O}_2\text{S}^*\text{C}_{12}\text{H}_8$   
 $\text{Li}_2\text{O}_2\text{S}^*\text{C}_{17}\text{H}_{14}$   
 $\text{Li}_2\text{O}_2\text{Se}^*\text{C}_8\text{H}_6$

$\text{Li}_2\text{O}_2\text{Si}^*\text{C}_5\text{H}_{10}$   
 $\text{Li}_2\text{O}_3^*\text{C}_5\text{H}_2$   
 $\text{Li}_2\text{O}_3^*\text{C}_5\text{H}_6$   
 $\text{Li}_2\text{O}_3\text{S}^*\text{C}_6\text{H}_4$   
 $\text{Li}_2\text{O}_3\text{S}^*\text{C}_9\text{H}_8$   
 $\text{Li}_2\text{O}_4^*\text{C}_{10}\text{H}_{12}$   
 $\text{Li}_2\text{O}_4^*\text{C}_{14}\text{H}_{10}$   
 $\text{Li}_2\text{O}_5\text{P}^*\text{C}_{16}\text{H}_{15}$   
 $\text{Li}_2\text{O}_5\text{Si}_4^*\text{C}_{28}\text{H}_{76}\text{Hg}$   
 $\text{Li}_2\text{Pb}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Li}_2\text{S}^*\text{C}_3\text{H}_4$   
 $\text{Li}_2\text{S}^*\text{C}_4\text{H}_2$   
 $\text{Li}_2\text{S}^*\text{C}_6\text{H}_4$   
 $\text{Li}_2\text{S}^*\text{C}_7\text{H}_6$   
 $\text{Li}_2\text{S}^*\text{C}_9\text{H}_6$   
 $\text{Li}_2\text{S}^*\text{C}_{12}\text{H}_8$   
 $\text{Li}_2\text{S}_2^*\text{C}_6\text{H}_8$   
 $\text{Li}_2\text{Se}^*\text{C}_9\text{H}_6$   
 **$\text{Li}_2\text{Si}$**

$\text{Li}_2\text{Si}$

Formation: 5.5.4.1

$\text{Li}_2\text{Si}^*\text{C}_{18}\text{H}_{18}$   
 $\text{Li}_2\text{Si}^*\text{C}_{30}\text{H}_{26}$   
 $\text{Li}_2\text{Si}_2^*\text{C}_{40}\text{H}_{36}$   
 $\text{Li}_2\text{Si}_4^*\text{C}_{48}\text{H}_{40}$   
 $\text{Li}_2\text{Si}_5^*\text{C}_{60}\text{H}_{50}$   
 $\text{Li}_2\text{Si}_6^*\text{C}_{72}\text{H}_{60}$

**$\text{Li}_2\text{Sn}$**

$\text{Li}_2\text{Sn}$

Formation: 5.5.6.1.1

$\text{Li}_2\text{Sn}^*\text{C}_{12}\text{H}_{10}$

**$\text{Li}_2\text{Sn}_5$**

$\text{Li}_2\text{Sn}_5$

Formation: 5.5.6.1.1

$\text{Li}_2\text{Zn}^*\text{C}_4\text{H}_{12}$

$\text{Li}_3^*\text{C}_3\text{H}$

$\text{Li}_3^*\text{C}_4\text{H}_3$

$\text{Li}_3^*\text{C}_5\text{H}_3$

$\text{Li}_3^*\text{C}_6\text{H}_8$

$\text{Li}_3^*\text{C}_7\text{H}_7$

$\text{Li}_3^*\text{C}_7\text{H}_9$

$\text{Li}_3^*\text{C}_8\text{H}_7$

$\text{Li}_3^*\text{C}_9\text{H}_9$

$\text{Li}_3^*\text{C}_{21}\text{H}_{17}$

$\text{Li}_3\text{N}^*\text{C}_6\text{H}_4$

$\text{Li}_3\text{O}_2\text{S}^*\text{C}_7\text{H}_5$

$\text{Li}_3\text{O}_4^*\text{C}_4\text{H}_3$

**$\text{Li}_3\text{Pb}$**

$\text{Li}_3\text{Pb}$

Formation: 5.5.7.1.1

**$\text{Li}_3\text{Sn}_2$**

$\text{Li}_3\text{Sn}_2$

Formation: 5.5.6.1.1

$\text{Li}_4^*\text{C}$	$\text{Mg}^*\text{CH}_2\text{DBr}$
$\text{Li}_4^*\text{C}_3$	$\text{Mg}^*\text{CH}_3\text{Br}$
$\text{Li}_4^*\text{C}_5$	$\text{Mg}^*\text{CH}_3\text{I}$
$\text{Li}_4^*\text{C}_6\text{H}_4$	$\text{Mg}^*\text{C}_2\text{H}_3\text{Br}$
$\text{Li}_4^*\text{C}_{14}\text{H}_{12}$	$\text{Mg}^*\text{C}_2\text{H}_5\text{Br}$
$\text{Li}_4^*\text{C}_{16}\text{H}_{10}$	$\text{Mg}^*\text{C}_3\text{H}_3\text{Br}$
$\text{Li}_4^*\text{C}_{28}\text{H}_{18}$	$\text{Mg}^*\text{C}_3\text{H}_5\text{Br}$
$\text{Li}_4^*\text{C}_{28}\text{H}_{22}$	$\text{Mg}^*\text{C}_3\text{H}_7\text{Br}$
$\text{Li}_4^*\text{Ge}$	$\text{Mg}^*\text{C}_3\text{H}_7\text{Cl}$
<b><math>\text{Li}_4\text{Pb}</math></b>	$\text{Mg}^*\text{C}_4\text{H}_3\text{Br}$
$\text{Li}_4\text{Pb}$	$\text{Mg}^*\text{C}_4\text{H}_7\text{Br}$
see $\text{Li}_{22}\text{Pb}_5$ ; 5.5.7.1.1	$\text{Mg}^*\text{C}_4\text{H}_7\text{Cl}$
<b><math>\text{Li}_4\text{Si}</math></b>	$\text{Mg}^*\text{C}_4\text{H}_9\text{Br}$
$\text{Li}_4\text{Si}$	$\text{Mg}^*\text{C}_4\text{H}_9\text{Cl}$
Formation: 5.5.4.1, 5.5.4.3	$\text{Mg}^*\text{C}_5\text{H}_{11}\text{Br}$
$\text{Li}_4\text{Si}^*\text{C}_{30}\text{H}_{26}$	$\text{Mg}^*\text{C}_5\text{H}_{12}\text{AsCl}$
<b><math>\text{Li}_4\text{Sn}</math></b>	$\text{Mg}^*\text{C}_6\text{BrCl}_5$
$\text{Li}_4\text{Sn}$	$\text{Mg}^*\text{C}_6\text{BrF}_5$
Formation: 5.5.6.1.1	$\text{Mg}^*\text{C}_6\text{D}_3\text{Br}$
<b><math>\text{Li}_5\text{Pb}_2</math></b>	$\text{Mg}^*\text{C}_6\text{H}_3\text{BrCl}_2$
$\text{Li}_5\text{Pb}_2$	$\text{Mg}^*\text{C}_6\text{H}_4\text{BrCl}$
see $\text{Li}_8\text{Pb}_3$ ; 5.5.7.1.1	$\text{Mg}^*\text{C}_6\text{H}_5\text{Br}$
<b><math>\text{Li}_5\text{Sn}_2</math></b>	$\text{Mg}^*\text{C}_6\text{H}_{11}\text{Br}$
$\text{Li}_5\text{Sn}_2$	$\text{Mg}^*\text{C}_7\text{H}_6\text{Cl}_2$
Formation: 5.5.6.1.1	$\text{Mg}^*\text{C}_7\text{H}_7\text{Br}$
$\text{Li}_6^*\text{C}_2$	$\text{Mg}^*\text{C}_7\text{H}_7\text{Cl}$
$\text{Li}_6^*\text{Ge}_2$	$\text{Mg}^*\text{C}_7\text{H}_{13}\text{Cl}$
<b><math>\text{Li}_7\text{Pb}_2</math></b>	$\text{Mg}^*\text{C}_8\text{H}_{17}\text{Br}$
$\text{Li}_7\text{Pb}_2$	$\text{Mg}^*\text{C}_{36}\text{H}_{30}\text{Cu}_4$
Formation: 5.5.7.1.1	$\text{MgO}^*\text{C}_5\text{H}_{11}\text{Cl}$
<b><math>\text{Li}_7\text{Sn}_2</math></b>	$\text{MgO}^*\text{C}_9\text{H}_9\text{Br}$
$\text{Li}_7\text{Sn}_2$	$\text{MgO}_2^*\text{C}_8\text{H}_9\text{Br}$
Formation: 5.5.6.1.1	$\text{MgS}^*\text{C}_5\text{H}_{11}\text{Cl}$
$\text{Li}_8^*\text{C}_3$	$\text{MgSi}^*\text{C}_4\text{H}_{11}\text{Cl}$
<b><math>\text{Li}_8\text{Pb}_3</math></b>	$\text{Mg}_2^*\text{C}_5\text{H}_{10}\text{Br}_2$
$\text{Li}_8\text{Pb}_3$	$\text{MnNO}_3^*\text{C}_{11}\text{H}_{11}\text{Li}$
Formation: 5.5.7.1.1	$\text{MnO}_3^*\text{C}_8\text{H}_4\text{Ag}$
<b><math>\text{Li}_{10}\text{Si}_3</math></b>	$\text{MnO}_3^*\text{C}_8\text{H}_4\text{BrHg}$
$\text{Li}_{10}\text{Si}_3$	$\text{MnO}_3^*\text{C}_8\text{H}_4\text{ClHg}$
Formation: 5.5.4.1	$\text{MnO}_3^*\text{C}_8\text{H}_4\text{Cu}$
<b><math>\text{Li}_{17}\text{Pb}_{83}</math></b>	$\text{MnO}_5^*\text{C}_8\text{H}_6\text{B}$
$\text{Li}_{17}\text{Pb}_{83}$	$\text{MnO}_5^*\text{C}_{15}\text{H}_9\text{ClFeHg}$
Formation: 5.5.7.1	$\text{MnO}_5^*\text{C}_{15}\text{H}_{10}\text{Fe}$
<b><math>\text{Li}_{17}\text{Si}_2</math></b>	$\text{MnO}_6^*\text{C}_{16}\text{H}_8\text{AgCu}$
$\text{Li}_{17}\text{Si}_2$	$\text{MoO}_4\text{S}^*\text{C}_{21}\text{H}_{15}\text{Li}$
Formation: 5.5.4.1	$\text{N}^*\text{CCu}$
<b><math>\text{Li}_{22}\text{Pb}_5</math></b>	$\text{N}^*\text{CK}$
$\text{Li}_{22}\text{Pb}_5$	$\text{N}^*\text{C}_2\text{HLi}_2$
Formation: 5.5.7.1.1	$\text{N}^*\text{C}_2\text{H}_2\text{ClHg}$
<b><math>\text{Li}_{22}\text{Sn}_5</math></b>	$\text{N}^*\text{C}_2\text{H}_2\text{Li}$
$\text{Li}_{22}\text{Sn}_5$	$\text{N}^*\text{C}_3\text{H}_3\text{D}_2\text{Hg}$
Formation: 5.5.6.1.1	$\text{N}^*\text{C}_3\text{H}_4\text{Li}$

N*C <sub>3</sub> H <sub>5</sub> Hg	N*C <sub>11</sub> H <sub>10</sub> Li
N*C <sub>3</sub> H <sub>8</sub> Li	N*C <sub>11</sub> H <sub>13</sub> Li <sub>2</sub>
N*C <sub>4</sub> H <sub>4</sub> Li	N*C <sub>12</sub> H <sub>10</sub> FeLi
N*C <sub>4</sub> H <sub>6</sub> Li	N*C <sub>12</sub> H <sub>10</sub> Li
N*C <sub>5</sub> Cl <sub>4</sub> Li	N*C <sub>12</sub> H <sub>13</sub> FeLi <sub>2</sub>
N*C <sub>5</sub> H <sub>3</sub> AgF <sub>7</sub>	N*C <sub>12</sub> H <sub>14</sub> FeLi
N*C <sub>5</sub> H <sub>3</sub> BrLi	N*C <sub>12</sub> H <sub>14</sub> Li
N*C <sub>5</sub> H <sub>3</sub> Li <sub>2</sub>	N*C <sub>12</sub> H <sub>15</sub> Br <sub>2</sub> Hg <sub>2</sub>
N*C <sub>5</sub> H <sub>4</sub> Li	N*C <sub>13</sub> H <sub>16</sub> ClFeHg
N*C <sub>5</sub> H <sub>5</sub> Li <sub>2</sub>	N*C <sub>13</sub> H <sub>16</sub> FeLi
N*C <sub>5</sub> H <sub>9</sub> Hg <sub>3</sub>	N*C <sub>13</sub> H <sub>16</sub> Li
N*C <sub>6</sub> H <sub>4</sub> Li <sub>3</sub>	N*C <sub>14</sub> H <sub>12</sub> Li
N*C <sub>6</sub> H <sub>6</sub> Li	N*C <sub>14</sub> H <sub>13</sub> BrHgLi
N*C <sub>6</sub> H <sub>11</sub> BrLi	N*C <sub>14</sub> H <sub>13</sub> Li <sub>2</sub>
N*C <sub>6</sub> H <sub>12</sub> Cs	N*C <sub>14</sub> H <sub>18</sub> FeLi
N*C <sub>6</sub> H <sub>12</sub> Li	N*C <sub>14</sub> H <sub>30</sub> Li
N*C <sub>6</sub> H <sub>14</sub> ClHg	N*C <sub>15</sub> H <sub>11</sub> Hg
N*C <sub>6</sub> H <sub>14</sub> Cs	N*C <sub>16</sub> H <sub>12</sub> Li
N*C <sub>6</sub> H <sub>14</sub> K	N*C <sub>17</sub> H <sub>18</sub> Li
N*C <sub>7</sub> F <sub>5</sub> Hg	N*C <sub>18</sub> H <sub>15</sub>
N*C <sub>7</sub> H <sub>3</sub> ClLi	N*C <sub>19</sub> H <sub>15</sub>
N*C <sub>7</sub> H <sub>4</sub> Li	N*C <sub>19</sub> H <sub>15</sub> Li <sub>2</sub>
N*C <sub>7</sub> H <sub>12</sub> Li	N*C <sub>19</sub> H <sub>22</sub> Li
N*C <sub>7</sub> H <sub>13</sub> Li <sub>2</sub>	N*C <sub>20</sub> H <sub>18</sub> Li
N*C <sub>8</sub> H <sub>5</sub> BrLi	N*C <sub>23</sub> H <sub>17</sub> Li
N*C <sub>8</sub> H <sub>6</sub> Li	N*C <sub>23</sub> H <sub>17</sub> Li <sub>2</sub>
N*C <sub>8</sub> H <sub>8</sub> Li	N*C <sub>39</sub> H <sub>34</sub> Cu
N*C <sub>8</sub> H <sub>9</sub> BrHgLi	N*C <sub>44</sub> H <sub>36</sub> AuBrF <sub>15</sub>
N*C <sub>8</sub> H <sub>9</sub> Li <sub>2</sub>	N*ClH <sub>2</sub> Hg
N*C <sub>8</sub> H <sub>10</sub> Ag	N*H <sub>3</sub>
N*C <sub>8</sub> H <sub>10</sub> Cu	NNa*C <sub>6</sub> H <sub>14</sub>
N*C <sub>8</sub> H <sub>10</sub> Li	NNa*H <sub>2</sub>
N*C <sub>8</sub> H <sub>14</sub> Li	NNaSi <sub>2</sub> *C <sub>6</sub> H <sub>18</sub>
N*C <sub>8</sub> H <sub>16</sub> ClHg	NO*C <sub>3</sub> H <sub>5</sub> Li <sub>2</sub>
N*C <sub>9</sub> H <sub>5</sub> Hg	NO*C <sub>3</sub> H <sub>6</sub> Li
N*C <sub>9</sub> H <sub>6</sub> Li	NO*C <sub>4</sub> H <sub>4</sub> Li
N*C <sub>9</sub> H <sub>10</sub> Li	NO*C <sub>4</sub> H <sub>8</sub> Li
N*C <sub>9</sub> H <sub>11</sub>	NO*C <sub>4</sub> H <sub>9</sub> Li <sub>2</sub>
N*C <sub>9</sub> H <sub>11</sub> BrHgLi	NO*C <sub>5</sub> H <sub>10</sub> Li
N*C <sub>9</sub> H <sub>11</sub> ClLi	NO*C <sub>6</sub> H <sub>8</sub> Li
N*C <sub>9</sub> H <sub>11</sub> Li <sub>2</sub>	NO*C <sub>7</sub> H <sub>5</sub> Hg
N*C <sub>9</sub> H <sub>12</sub> Ag	NO*C <sub>7</sub> H <sub>14</sub> Li
N*C <sub>9</sub> H <sub>12</sub> Ag <sub>2</sub> Br	NO*C <sub>8</sub> H <sub>7</sub> Hg
N*C <sub>9</sub> H <sub>12</sub> ClHg	NO*C <sub>8</sub> H <sub>7</sub> Li <sub>2</sub>
N*C <sub>9</sub> H <sub>12</sub> Li	NO*C <sub>8</sub> H <sub>13</sub> Li <sub>2</sub>
N*C <sub>9</sub> H <sub>13</sub> AuBr <sub>3</sub>	NO*C <sub>8</sub> H <sub>14</sub> ClHg
N*C <sub>10</sub> H <sub>7</sub> Li <sub>2</sub>	NO*C <sub>9</sub> H <sub>7</sub> Li <sub>2</sub>
N*C <sub>10</sub> H <sub>10</sub> Li	NO*C <sub>9</sub> H <sub>9</sub> Li <sub>2</sub>
N*C <sub>10</sub> H <sub>12</sub> Li	NO*C <sub>9</sub> H <sub>14</sub> Li
N*C <sub>10</sub> H <sub>14</sub> Li	NO*C <sub>9</sub> H <sub>16</sub> ClHg
N*C <sub>10</sub> H <sub>18</sub> Li	NO*C <sub>10</sub> H <sub>12</sub> ClLi <sub>2</sub>
N*C <sub>10</sub> H <sub>21</sub> GeHg	NO*C <sub>10</sub> H <sub>13</sub> Li <sub>2</sub>

- $\text{NO}^*\text{C}_{10}\text{H}_{14}\text{Li}$   
 $\text{NO}^*\text{C}_{11}\text{H}_{12}\text{Li}$   
 $\text{NO}^*\text{C}_{11}\text{H}_{13}\text{Li}_2$   
 $\text{NO}^*\text{C}_{11}\text{H}_{14}\text{Li}$   
 $\text{NO}^*\text{C}_{12}\text{H}_{15}\text{Li}_2$   
 $\text{NO}^*\text{C}_{13}\text{H}_{16}\text{Li}$   
 $\text{NO}^*\text{C}_{14}\text{H}_{11}\text{Li}_2$   
 $\text{NO}^*\text{C}_{15}\text{H}_{10}\text{Li}$   
 $\text{NO}^*\text{C}_{18}\text{H}_{28}\text{Li}$   
 $\text{NO}^*\text{C}_{19}\text{H}_{30}\text{Li}$   
 $\text{NO}^*\text{C}_{20}\text{H}_{32}\text{Li}$   
 $\text{NO}^*\text{C}_{21}\text{H}_{22}\text{Li}$   
 $\text{NOS}^*\text{C}_3\text{H}_8\text{Li}$   
 $\text{NOS}^*\text{C}_7\text{H}_{12}\text{Li}$   
 $\text{NOS}^*\text{C}_8\text{H}_8\text{Li}$   
 $\text{NOS}^*\text{C}_8\text{H}_9\text{Li}_2$   
 $\text{NOS}^*\text{C}_8\text{H}_{10}\text{Li}$   
 $\text{NOS}_2^*\text{C}_7\text{H}_{12}\text{Li}$   
 $\text{NOSi}^*\text{C}_7\text{H}_{14}\text{Li}$   
 $\text{NOSi}^*\text{C}_7\text{H}_{16}\text{Li}$   
 $\text{NOSi}^*\text{C}_8\text{H}_{14}\text{Li}$   
 $\text{NOSi}^*\text{C}_{11}\text{H}_{14}\text{Li}$   
 $\text{NOSn}^*\text{C}_{16}\text{H}_{37}$   
 $\text{NOZn}^*\text{C}_6\text{H}_{12}\text{Br}$   
 $\text{NO}_2^*\text{C}_2\text{H}_4\text{Li}_2$   
 $\text{NO}_2^*\text{C}_3\text{H}_2\text{Cu}$   
 $\text{NO}_2^*\text{C}_3\text{H}_4\text{Li}_2$   
 $\text{NO}_2^*\text{C}_4\text{H}_5\text{Hg}$   
 $\text{NO}_2^*\text{C}_4\text{H}_6\text{Li}$   
 $\text{NO}_2^*\text{C}_5\text{H}_3\text{F}_6\text{Hg}$   
 $\text{NO}_2^*\text{C}_6\text{H}_4\text{BrHg}$   
 $\text{NO}_2^*\text{C}_6\text{H}_4\text{ClHg}$   
 $\text{NO}_2^*\text{C}_6\text{H}_4\text{HgI}$   
 $\text{NO}_2^*\text{C}_6\text{H}_4\text{Li}$   
 $\text{NO}_2^*\text{C}_6\text{H}_5$   
 $\text{NO}_2^*\text{C}_6\text{H}_5\text{Li}$   
 $\text{NO}_2^*\text{C}_6\text{H}_{10}\text{ClHg}$   
 $\text{NO}_2^*\text{C}_6\text{H}_{12}\text{Li}$   
 $\text{NO}_2^*\text{C}_7\text{H}_6\text{Li}$   
 $\text{NO}_2^*\text{C}_9\text{H}_{11}\text{Hg}$   
 $\text{NO}_2^*\text{C}_9\text{H}_{12}\text{Li}$   
 $\text{NO}_2^*\text{C}_9\text{H}_{14}\text{Li}$   
 $\text{NO}_2^*\text{C}_{11}\text{H}_{13}\text{Li}_2$   
 $\text{NO}_2^*\text{C}_{12}\text{H}_{14}\text{Li}$   
 $\text{NO}_2^*\text{C}_{12}\text{H}_{16}\text{Li}$   
 $\text{NO}_2^*\text{C}_{20}\text{H}_{33}\text{Hg}$   
 $\text{NO}_2\text{P}^*\text{C}_{17}\text{H}_{19}\text{Li}$   
 $\text{NO}_2\text{P}^*\text{C}_{23}\text{H}_{21}\text{Au}$   
 $\text{NO}_2\text{S}^*\text{C}_3\text{H}_7\text{Li}_2$   
 $\text{NO}_2\text{S}^*\text{C}_3\text{H}_8\text{Li}$   
 $\text{NO}_2\text{S}^*\text{C}_5\text{H}_{10}\text{Li}$   
 $\text{NO}_2\text{S}^*\text{C}_6\text{H}_6\text{ClHg}$   
 $\text{NO}_2\text{S}^*\text{C}_8\text{H}_{10}\text{Li}$   
 $\text{NO}_2\text{S}^*\text{C}_9\text{H}_7\text{Li}_2$   
 $\text{NO}_2\text{S}^*\text{C}_{12}\text{H}_{14}\text{Li}$   
 $\text{NO}_2\text{S}^*\text{C}_{16}\text{H}_{18}\text{Li}$   
 $\text{NO}_3^*\text{Ag}$   
 $\text{NO}_3^*\text{CH}_3\text{Ag}_2$   
 $\text{NO}_3^*\text{C}_5\text{H}_{10}\text{Li}$   
 $\text{NO}_3^*\text{C}_6\text{H}_5\text{Hg}$   
 $\text{NO}_3^*\text{C}_8\text{H}_6\text{ClHg}$   
 $\text{NO}_3^*\text{C}_8\text{H}_9\text{Hg}_3$   
 $\text{NO}_3^*\text{C}_{10}\text{H}_{11}\text{Hg}$   
 $\text{NO}_3^*\text{C}_{11}\text{H}_{11}\text{LiMn}$   
 $\text{NO}_3^*\text{C}_{14}\text{H}_{20}\text{Li}$   
 $\text{NO}_3^*\text{C}_{14}\text{H}_{26}\text{ClHg}$   
 $\text{NO}_3^*\text{C}_{15}\text{H}_{20}\text{Li}$   
 $\text{NO}_3\text{P}^*\text{C}_6\text{H}_{11}\text{Li}$   
 $\text{NO}_3\text{P}^*\text{C}_8\text{H}_{15}\text{Li}$   
 $\text{NO}_3\text{P}^*\text{C}_9\text{H}_{19}\text{Li}$   
 $\text{NO}_3\text{S}^*\text{C}_9\text{H}_{10}\text{Li}$   
 $\text{NO}_3\text{S}_2^*\text{C}_9\text{H}_{12}\text{Li}$   
 $\text{NO}_3\text{S}_2^*\text{C}_{14}\text{H}_{14}\text{Li}$   
 $\text{NO}_4^*\text{C}_8\text{H}_7\text{Hg}$   
 $\text{NO}_4^*\text{C}_9\text{H}_{19}\text{Hg}$   
 $\text{NO}_4^*\text{C}_{10}\text{H}_{11}\text{Hg}_2$   
 $\text{NO}_4^*\text{C}_{11}\text{H}_{23}\text{Hg}$   
 $\text{NO}_5^*\text{C}_8\text{H}_8\text{B}$   
 $\text{NO}_6^*\text{C}_3\text{H}_6\text{ClHg}$   
 $\text{NO}_{12}^*\text{C}_{16}\text{F}_{15}\text{Hg}_5$   
 $\text{NP}^*\text{C}_{20}\text{H}_{32}\text{Cu}$   
 $\text{NP}^*\text{C}_{27}\text{H}_{27}\text{Au}$   
 $\text{NP}_1^*\text{C}_6\text{H}_{16}\text{Li}$   
 $\text{NP}_2^*\text{C}_{38}\text{H}_{32}\text{Cu}$   
 $\text{NS}^*\text{CCu}$   
 $\text{NS}^*\text{C}_3\text{HILi}$   
 $\text{NS}^*\text{C}_3\text{H}_2\text{ClHg}$   
 $\text{NS}^*\text{C}_3\text{H}_2\text{Li}$   
 $\text{NS}^*\text{C}_3\text{H}_6\text{Li}$   
 $\text{NS}^*\text{C}_5\text{H}_6\text{Li}$   
 $\text{NS}^*\text{C}_5\text{H}_8\text{Li}$   
 $\text{NS}^*\text{C}_6\text{H}_{14}\text{Li}$   
 $\text{NS}^*\text{C}_7\text{H}_{14}\text{Li}$   
 $\text{NS}^*\text{C}_8\text{H}_6\text{Li}$   
 $\text{NS}^*\text{C}_8\text{H}_7\text{Li}_2$   
 $\text{NS}^*\text{C}_8\text{H}_8\text{Li}$   
 $\text{NS}^*\text{C}_9\text{H}_9\text{Li}_2$   
 $\text{NS}^*\text{C}_{11}\text{H}_{14}\text{Li}$   
 $\text{NSSi}^*\text{C}_7\text{H}_{16}\text{Li}$   
 $\text{NS}_1^*\text{C}_4\text{H}_6\text{Li}$   
 $\text{NS}_2^*\text{C}_4\text{H}_8\text{Li}$   
 $\text{NS}_2^*\text{C}_5\text{H}_6\text{Li}$   
 $\text{NS}_2^*\text{C}_6\text{H}_{10}\text{Li}$   
 $\text{NS}_2^*\text{C}_9\text{H}_{10}\text{Li}$

$\text{NS}_3^*\text{C}_5\text{H}_{10}\text{Li}$	$\text{N}_2^*\text{C}_{18}\text{H}_{24}\text{Hg}$
$\text{NSe}^*\text{C}_5\text{H}_2\text{Li}$	$\text{N}_2^*\text{C}_{28}\text{H}_{36}\text{Fe}_2\text{Hg}$
$\text{NSe}^*\text{C}_{14}\text{H}_{18}\text{Li}$	$\text{N}_2^*\text{C}_{36}\text{H}_{40}\text{Br}_2\text{Cu}_4$
$\text{NSi}^*\text{C}_5\text{H}_{10}\text{Li}$	$\text{N}_2^*\text{C}_{39}\text{H}_{30}\text{Au}_2$
$\text{NSi}^*\text{C}_7\text{H}_7\text{Cl}_4$	$\text{N}_2^*\text{C}_{39}\text{H}_{31}\text{Cu}$
$\text{NSi}^*\text{C}_7\text{H}_{15}$	$\text{N}_2\text{O}^*\text{C}_2\text{H}_3\text{Li}$
$\text{NSi}^*\text{C}_{11}\text{H}_{27}$	$\text{N}_2\text{O}^*\text{C}_3\text{H}_3\text{Li}$
$\text{NSi}^*\text{C}_{16}\text{H}_{17}$	$\text{N}_2\text{O}^*\text{C}_3\text{H}_5\text{Li}$
$\text{NSi}_2^*\text{C}_6\text{H}_{19}$	$\text{N}_2\text{O}^*\text{C}_4\text{H}_6\text{Hg}$
$\text{NSi}_2^*\text{C}_7\text{H}_{21}\text{Hg}$	$\text{N}_2\text{O}^*\text{C}_4\text{H}_7\text{Li}$
$\text{NSi}_2^*\text{C}_{11}\text{H}_{23}\text{Hg}$	$\text{N}_2\text{O}^*\text{C}_6\text{H}_{19}\text{Li}$
$\text{NSn}^*\text{C}_{15}\text{H}_{35}$	$\text{N}_2\text{O}^*\text{C}_{11}\text{H}_{19}\text{Li}$
$\text{NSn}^*\text{C}_{18}\text{H}_{39}$	$\text{N}_2\text{OP}^*\text{C}_5\text{H}_{13}\text{ClLi}$
$\text{NSn}^*\text{C}_{21}\text{H}_{37}$	$\text{N}_2\text{OP}^*\text{C}_5\text{H}_{14}\text{Li}$
$\text{NSn}^*\text{C}_{21}\text{H}_{39}$	$\text{N}_2\text{OP}^*\text{C}_7\text{H}_{16}\text{Li}$
$\text{NSn}^*\text{C}_{35}\text{H}_{33}$	$\text{N}_2\text{OP}^*\text{C}_8\text{H}_{19}\text{Li}$
$\text{NSn}^*\text{C}_{37}\text{H}_{37}$	$\text{N}_2\text{O}_2^*\text{C}_2\text{Hg}$
$\text{NZn}^*\text{C}_{13}\text{H}_{28}\text{Cl}_2\text{F}_3$	$\text{N}_2\text{O}_2^*\text{C}_4\text{H}_5\text{Li}$
$\text{NZn}^*\text{C}_{13}\text{H}_{31}\text{Cl}_2$	$\text{N}_2\text{O}_2^*\text{C}_4\text{H}_6\text{Hg}$
$\text{NZn}^*\text{C}_{14}\text{H}_{33}\text{Cl}_2$	$\text{N}_2\text{O}_2^*\text{C}_{20}\text{H}_{24}\text{Hg}$
$\text{NZn}^*\text{C}_{18}\text{H}_{33}\text{Cl}_2$	$\text{N}_2\text{O}_2\text{P}^*\text{C}_7\text{H}_{16}\text{Li}$
$\text{N}_2^*\text{CH}_2$	$\text{N}_2\text{O}_2\text{S}^*\text{C}_{11}\text{H}_{13}\text{Li}_2$
$\text{N}_2^*\text{C}_2\text{Hg}$	$\text{N}_2\text{O}_4^*\text{C}_8\text{H}_{14}\text{Hg}$
$\text{N}_2^*\text{C}_3\text{Cl}_2\text{Hg}_2$	$\text{N}_2\text{O}_4^*\text{C}_{12}\text{Cl}_8\text{Hg}$
$\text{N}_2^*\text{C}_4\text{H}_4\text{Hg}$	$\text{N}_2\text{O}_4^*\text{C}_{12}\text{F}_8\text{Hg}$
$\text{N}_2^*\text{C}_4\text{H}_5\text{Li}$	$\text{N}_2\text{O}_4^*\text{C}_{12}\text{H}_8\text{Hg}$
$\text{N}_2^*\text{C}_5\text{H}_7\text{Li}$	$\text{N}_2\text{O}_4\text{P}_2^*\text{C}_{42}\text{H}_{35}\text{Cu}$
$\text{N}_2^*\text{C}_5\text{H}_{11}\text{Li}$	$\text{N}_2\text{O}_6^*\text{Hg}$
$\text{N}_2^*\text{C}_6\text{H}_9\text{Li}$	$\text{N}_2\text{O}_6\text{S}_2^*\text{C}_{22}\text{H}_{10}\text{F}_{10}\text{Hg}$
$\text{N}_2^*\text{C}_6\text{H}_{11}\text{Li}$	$\text{N}_2\text{O}_6\text{S}_2^*\text{C}_{22}\text{H}_{10}\text{Hg}$
$\text{N}_2^*\text{C}_6\text{H}_{13}\text{Li}$	$\text{N}_2\text{O}_6\text{S}_2^*\text{C}_{22}\text{H}_{12}\text{Cl}_8\text{Hg}$
$\text{N}_2^*\text{C}_7\text{H}_7\text{Li}$	$\text{N}_2\text{O}_6\text{S}_2^*\text{C}_{22}\text{H}_{12}\text{F}_8\text{Hg}$
$\text{N}_2^*\text{C}_7\text{H}_9\text{Li}$	$\text{N}_2\text{O}_7^*\text{C}_{10}\text{H}_{21}\text{Hg}$
$\text{N}_2^*\text{C}_7\text{H}_{11}\text{Li}$	$\text{N}_2\text{O}_8^*\text{C}_{14}\text{H}_8\text{Hg}$
$\text{N}_2^*\text{C}_8\text{F}_{12}\text{Hg}$	$\text{N}_2\text{Pb}^*\text{Cl}_6\text{Hg}$
$\text{N}_2^*\text{C}_8\text{H}_{12}\text{Hg}$	$\text{N}_2\text{S}_2^*\text{C}_2\text{Cd}$
$\text{N}_2^*\text{C}_9\text{H}_7\text{Li}$	$\text{N}_2\text{S}_4^*\text{C}_{11}\text{H}_{21}\text{Li}$
$\text{N}_2^*\text{C}_9\text{H}_8\text{Li}_2$	$\text{N}_2\text{Si}^*\text{C}_4\text{H}_9\text{Li}$
$\text{N}_2^*\text{C}_{10}\text{F}_8\text{Hg}$	$\text{N}_2\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{Cd}$
$\text{N}_2^*\text{C}_{10}\text{H}_8\text{Li}$	$\text{N}_2\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{Hg}$
$\text{N}_2^*\text{C}_{10}\text{H}_{10}\text{Hg}$	$\text{N}_2\text{Si}_4\text{Zn}^*\text{C}_{12}\text{H}_{36}$
$\text{N}_2^*\text{C}_{11}\text{H}_{11}\text{Li}$	$\text{N}_2\text{Sn}_2\text{Zn}^*\text{C}_{36}\text{H}_{36}$
$\text{N}_2^*\text{C}_{11}\text{H}_{15}\text{Li}$	$\text{N}_2\text{Zn}^*\text{C}_{16}\text{H}_{20}$
$\text{N}_2^*\text{C}_{13}\text{H}_{24}\text{GeHg}$	$\text{N}_2\text{Zn}^*\text{C}_{18}\text{H}_{24}$
$\text{N}_2^*\text{C}_{15}\text{H}_{15}\text{Li}$	$\text{N}_3^*\text{C}_6\text{F}_5\text{Hg}$
$\text{N}_2^*\text{C}_{15}\text{H}_{17}\text{BrHg}$	$\text{N}_3^*\text{C}_6\text{H}_{10}\text{ClHg}$
$\text{N}_2^*\text{C}_{16}\text{H}_{12}\text{Hg}$	$\text{N}_3^*\text{C}_8\text{H}_6\text{Li}$
$\text{N}_2^*\text{C}_{16}\text{H}_{20}\text{Hg}$	$\text{N}_3^*\text{C}_{15}\text{H}_{12}\text{Au}_3$
$\text{N}_2^*\text{C}_{18}\text{H}_{13}\text{Cu}$	$\text{N}_3^*\text{C}_{15}\text{H}_{12}\text{Li}$
$\text{N}_2^*\text{C}_{18}\text{H}_{20}\text{Cu}_2$	$\text{N}_3\text{Na}^*\text{C}_{18}\text{H}_{24}\text{Ge}$
$\text{N}_2^*\text{C}_{18}\text{H}_{24}\text{Au}_2$	$\text{N}_3\text{OP}^*\text{C}_6\text{H}_{17}\text{Li}$
$\text{N}_2^*\text{C}_{18}\text{H}_{24}\text{CuLi}$	$\text{N}_3\text{OP}^*\text{C}_{12}\text{H}_{19}\text{Li}$



$\text{N}_3\text{OP}^*\text{C}_{12}\text{H}_{21}\text{Li}$   
 $\text{N}_3\text{O}_3^*\text{C}_5\text{H}_9\text{Cr}$   
 $\text{N}_3\text{O}_3^*\text{C}_{30}\text{H}_{36}\text{Ag}_3$   
 $\text{N}_3\text{O}_3^*\text{C}_{30}\text{H}_{36}\text{Au}_3$   
 $\text{N}_3\text{O}_3^*\text{C}_{33}\text{H}_{36}\text{Ag}_3$   
 $\text{N}_4^*\text{Au}_2\text{C}_{36}\text{H}_{40}\text{Li}_2$   
 $\text{N}_4^*\text{C}_2\text{H}_3\text{Li}$   
 $\text{N}_4^*\text{C}_4\text{F}_6\text{Hg}$   
 $\text{N}_4^*\text{C}_6\text{H}_3\text{Hg}$   
 $\text{N}_4^*\text{C}_{12}\text{H}_9\text{Li}$   
 $\text{N}_4^*\text{C}_{12}\text{H}_{10}\text{Li}$   
 $\text{N}_4^*\text{C}_{14}\text{H}_{18}\text{Hg}$   
 $\text{N}_4^*\text{C}_{22}\text{H}_{30}\text{Cu}_2$   
 $\text{N}_4^*\text{C}_{32}\text{H}_{40}\text{Br}_2\text{Cu}_6$   
 $\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Ag}_2\text{Li}_2$   
 $\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Au}_2\text{Li}_2$   
 $\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Cu}_2\text{Li}_2$   
 $\text{N}_4^*\text{C}_{36}\text{H}_{48}\text{Cu}_4$   
 $\text{N}_4^*\text{C}_{40}\text{H}_{56}\text{Cu}_4$   
 $\text{N}_4^*\text{C}_{50}\text{H}_{54}\text{Cu}_6$   
 $\text{N}_4\text{O}_2^*\text{C}_{12}\text{H}_{18}\text{Hg}$   
 $\text{N}_4\text{O}_2\text{P}_2^*\text{C}_{26}\text{H}_{20}\text{Hg}$   
 $\text{N}_4\text{O}_4^*\text{C}_8\text{H}_{10}\text{Cd}$   
 $\text{N}_4\text{O}_4^*\text{C}_6\text{H}_{10}\text{Hg}$   
 $\text{N}_4\text{O}_4\text{Zn}^*\text{C}_8\text{H}_{10}$   
 $\text{N}_4\text{O}_6\text{S}_2^*\text{C}_{34}\text{H}_{40}\text{Ag}_4\text{Au}_2\text{F}_6$   
 $\text{N}_4\text{O}_8^*\text{C}_2\text{F}_2\text{Hg}$   
 $\text{N}_6^*\text{C}_5\text{H}_8\text{Hg}$   
 $\text{N}_6^*\text{Hg}$   
 $\text{N}_6\text{O}_{12}^*\text{C}_2\text{Hg}$   
 $\text{N}_6\text{O}_{12}^*\text{C}_4\text{H}_4\text{Hg}$   
 $\text{N}_6\text{O}_{12}^*\text{C}_{12}\text{H}_4\text{Hg}$   
 $\text{N}_6\text{O}_{16}^*\text{C}_{14}\text{H}_4\text{Hg}$

**Na**

## Na

Reaction with  $\text{R}_3\text{PbX}$ : 5.5.7.4  
 Reaction with  $\text{R}_4\text{Pb}$ : 5.5.7.3  
 Reaction with  $(\text{R}_3\text{Pb})_2$ : 5.5.7.2.1  
 Reaction with  $(\text{R}_3\text{Sn})_2$ : 5.5.6.2.2  
 Reaction with  $\text{CH}\equiv\text{CH}$ : 5.5.3.1.1

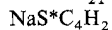
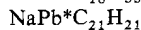
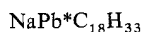
$\text{Na}^*\text{CHBr}_2$   
 $\text{Na}^*\text{CH}_3$   
 $\text{Na}^*\text{CH}_5\text{Ge}$   
 $\text{Na}^*\text{C}_2\text{H}$   
 $\text{Na}^*\text{C}_2\text{H}_5$   
 $\text{Na}^*\text{C}_2\text{H}_7\text{Ge}$   
 $\text{Na}^*\text{C}_3\text{H}_5$   
 $\text{Na}^*\text{C}_4\text{H}_9$   
 $\text{Na}^*\text{C}_5\text{H}_5$   
 $\text{Na}^*\text{C}_5\text{H}_{11}$   
 $\text{Na}^*\text{C}_6\text{H}_5$   
 $\text{Na}^*\text{C}_6\text{H}_{14}\text{N}$

$\text{Na}^*\text{C}_6\text{H}_{15}\text{Ge}$   
 $\text{Na}^*\text{C}_7\text{H}_7$   
 $\text{Na}^*\text{C}_7\text{H}_9$   
 $\text{Na}^*\text{C}_7\text{H}_{13}$   
 $\text{Na}^*\text{C}_8\text{H}_5$   
 $\text{Na}^*\text{C}_8\text{H}_9$   
 $\text{Na}^*\text{C}_8\text{H}_{20}\text{Al}$   
 $\text{Na}^*\text{C}_{10}\text{H}_8$   
 $\text{Na}^*\text{C}_{11}\text{H}_9$   
 $\text{Na}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Na}^*\text{C}_{12}\text{H}_{23}$   
 $\text{Na}^*\text{C}_{12}\text{H}_{27}\text{Ge}$   
 $\text{Na}^*\text{C}_{13}\text{H}_{11}$   
 $\text{Na}^*\text{C}_{14}\text{H}_{10}$   
 $\text{Na}^*\text{C}_{14}\text{H}_{13}$   
 $\text{Na}^*\text{C}_{18}\text{H}_{15}\text{Ge}$   
 $\text{Na}^*\text{C}_{18}\text{H}_{24}\text{GeN}_3$   
 $\text{Na}^*\text{C}_{19}\text{H}_{15}$   
 $\text{Na}^*\text{C}_{19}\text{H}_{23}$   
 $\text{Na}^*\text{C}_{20}\text{H}_{17}$   
 $\text{Na}^*\text{C}_{21}\text{H}_{15}$   
 $\text{Na}^*\text{C}_{21}\text{H}_{19}$   
 $\text{Na}^*\text{C}_{23}\text{H}_{21}$   
 $\text{Na}^*\text{C}_{25}\text{H}_{19}$   
 $\text{Na}^*\text{C}_{64}$   
 $\text{Na}^*\text{Cl}$   
 $\text{Na}^*\text{F}$   
 $\text{Na}^*\text{Ge}$   
 $\text{Na}^*\text{GeH}_3$   
 $\text{Na}^*\text{H}$   
 $\text{Na}^*\text{H}_2\text{N}$   
 $\text{Na}^*\text{Hg}$   
 $\text{Na}^*\text{K}$   
 $\text{NaO}^*\text{CH}_3$   
 $\text{NaO}^*\text{C}_4\text{H}_9$   
 $\text{NaO}^*\text{C}_6\text{H}_{13}$   
 $\text{NaO}^*\text{C}_8\text{H}_7$   
 $\text{NaO}^*\text{H}$   
 $\text{NaOS}^*\text{C}_2\text{H}_5$   
 $\text{NaOSi}^*\text{C}_3\text{H}_9$   
 $\text{NaO}_2^*\text{C}_5\text{H}_8\text{Cl}$   
 $\text{NaO}_2\text{Si}^*\text{C}_3\text{H}_9$   
 $\text{NaO}_3\text{Pb}^*\text{C}_{21}\text{H}_{21}$   
 $\text{NaO}_3\text{Pb}^*\text{C}_{24}\text{H}_{27}$   
**NaPb**

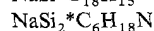
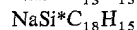
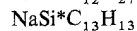
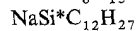
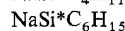
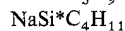
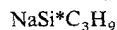
## NaPb

Formation: 5.5.7.1.1, 5.5.7.1.2

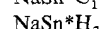
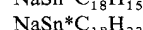
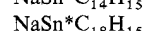
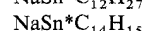
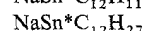
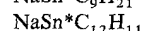
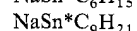
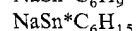
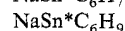
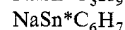
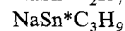
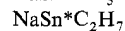
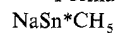
$\text{NaPb}^*\text{C}_3\text{H}_9$   
 $\text{NaPb}^*\text{C}_6\text{H}_9$   
 $\text{NaPb}^*\text{C}_6\text{H}_{15}$   
 $\text{NaPb}^*\text{C}_{10}\text{H}_{15}$   
 $\text{NaPb}^*\text{C}_{18}\text{H}_{15}$

**NaSi**

Formation: 5.5.4.1

**NaSn**

Formation: 5.5.6.1.2

**NaSn<sub>2</sub>**

Formation: 5.5.6.1.2

**NaSn<sub>3</sub>**

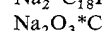
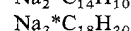
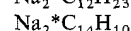
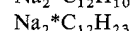
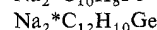
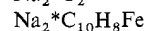
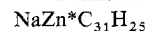
Formation: 5.5.6.1.2

**NaSn<sub>4</sub>**

Formation: 5.5.6.1.2

**NaSn<sub>6</sub>**

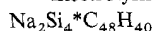
Formation: 5.5.6.1.2



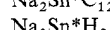
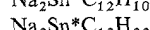
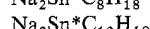
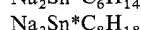
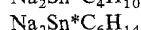
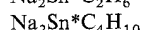
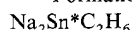
Electrolysis: 5.5.7.1.3

**Na<sub>2</sub>S**

Electrolysis: 5.5.7.1.3

**Na<sub>2</sub>Sn**

Formation: 5.5.6.1.2

**Na<sub>3</sub>Sn**

Formation: 5.5.6.1.2

**Na<sub>4</sub>Sn**

Formation: 5.5.6.1.2

**Na<sub>4</sub>Sn<sub>3</sub>**

Formation: 5.5.6.1.2

**Na<sub>4</sub>Sn<sub>9</sub>**

Formation: 5.5.6.1.2

**Na<sub>9</sub>Pb<sub>4</sub>**

Formation: 5.5.7.1.1

**Na<sub>15</sub>Pb<sub>4</sub>**

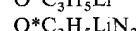
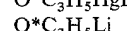
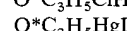
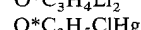
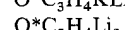
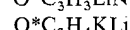
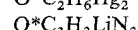
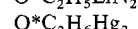
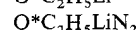
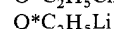
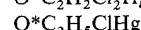
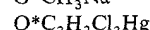
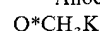
Formation: 5.5.7.1.1

**Na<sub>15</sub>Sn<sub>4</sub>**

Formation: 5.5.6.1.2

**Ni**

Anode: 5.5.7.1.3



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O*C <sub>3</sub> H <sub>5</sub> Li <sub>2</sub> N	O*C <sub>7</sub> H <sub>14</sub> LiN
O*C <sub>3</sub> H <sub>6</sub> LiN	O*C <sub>7</sub> H <sub>14</sub> Li <sub>2</sub>
O*C <sub>3</sub> H <sub>6</sub> Li <sub>2</sub>	O*C <sub>7</sub> H <sub>19</sub> Au
O*C <sub>3</sub> H <sub>7</sub> Li	O*C <sub>8</sub> H <sub>7</sub> HgI
O*C <sub>4</sub> H <sub>2</sub> BrLi	O*C <sub>8</sub> H <sub>7</sub> HgN
O*C <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub> Hg <sub>2</sub>	O*C <sub>8</sub> H <sub>7</sub> Li
O*C <sub>4</sub> H <sub>3</sub> ClHg	O*C <sub>8</sub> H <sub>7</sub> Li <sub>2</sub> N
O*C <sub>4</sub> H <sub>3</sub> Li	O*C <sub>8</sub> H <sub>7</sub> Na
O*C <sub>4</sub> H <sub>4</sub> ClLi	O*C <sub>8</sub> H <sub>8</sub> BrHgLi
O*C <sub>4</sub> H <sub>4</sub> LiN	O*C <sub>8</sub> H <sub>8</sub> Li <sub>2</sub>
O*C <sub>4</sub> H <sub>5</sub> Li	O*C <sub>8</sub> H <sub>9</sub> ClHg
O*C <sub>4</sub> H <sub>6</sub> BrLi	O*C <sub>8</sub> H <sub>9</sub> Li
O*C <sub>4</sub> H <sub>6</sub> ClLi	O*C <sub>8</sub> H <sub>13</sub> Li
O*C <sub>4</sub> H <sub>6</sub> HgN <sub>2</sub>	O*C <sub>8</sub> H <sub>13</sub> Li <sub>2</sub> N
O*C <sub>4</sub> H <sub>7</sub> HgI	O*C <sub>8</sub> H <sub>14</sub> ClHgN
O*C <sub>4</sub> H <sub>7</sub> Li	O*C <sub>8</sub> H <sub>16</sub> Li <sub>2</sub>
O*C <sub>4</sub> H <sub>7</sub> LiN <sub>2</sub>	O*C <sub>8</sub> H <sub>17</sub> Li
O*C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> Hg <sub>2</sub>	O*C <sub>8</sub> H <sub>20</sub> Ge
O*C <sub>4</sub> H <sub>8</sub> LiN	O*C <sub>9</sub> H <sub>4</sub> F <sub>6</sub> Li <sub>2</sub>
O*C <sub>4</sub> H <sub>9</sub> Cs	O*C <sub>9</sub> H <sub>7</sub> ClHg
O*C <sub>4</sub> H <sub>9</sub> K	O*C <sub>9</sub> H <sub>7</sub> Li <sub>2</sub> N
O*C <sub>4</sub> H <sub>9</sub> Li	O*C <sub>9</sub> H <sub>9</sub> BrMg
O*C <sub>4</sub> H <sub>9</sub> Li <sub>2</sub> N	O*C <sub>9</sub> H <sub>9</sub> ClHg
O*C <sub>4</sub> H <sub>9</sub> Na	O*C <sub>9</sub> H <sub>9</sub> Li <sub>2</sub> N
O*C <sub>4</sub> H <sub>12</sub> Ge	O*C <sub>9</sub> H <sub>10</sub> Li <sub>2</sub>
O*C <sub>5</sub> H <sub>7</sub> K	O*C <sub>9</sub> H <sub>11</sub> HgI
O*C <sub>5</sub> H <sub>7</sub> Li	O*C <sub>9</sub> H <sub>14</sub> LiN
O*C <sub>5</sub> H <sub>8</sub> BrLi	O*C <sub>9</sub> H <sub>15</sub> Li
O*C <sub>5</sub> H <sub>9</sub> Li	O*C <sub>9</sub> H <sub>16</sub> ClHgN
O*C <sub>5</sub> H <sub>10</sub> LiN	O*C <sub>9</sub> H <sub>16</sub> Li <sub>2</sub>
O*C <sub>5</sub> H <sub>10</sub> Li <sub>2</sub>	O*C <sub>9</sub> H <sub>17</sub> ClHg
O*C <sub>5</sub> H <sub>11</sub> ClMg	O*C <sub>9</sub> H <sub>17</sub> Li
O*C <sub>5</sub> H <sub>11</sub> Li	O*C <sub>9</sub> H <sub>18</sub> Li <sub>2</sub>
O*C <sub>6</sub> H <sub>4</sub> Li <sub>2</sub>	O*C <sub>9</sub> H <sub>19</sub> Li
O*C <sub>6</sub> H <sub>8</sub> LiN	O*C <sub>9</sub> H <sub>19</sub> LiN <sub>2</sub>
O*C <sub>6</sub> H <sub>9</sub> ClHg	O*C <sub>10</sub> H <sub>8</sub> Li <sub>2</sub>
O*C <sub>6</sub> H <sub>9</sub> Li	O*C <sub>10</sub> H <sub>12</sub> ClLi <sub>2</sub> N
O*C <sub>6</sub> H <sub>10</sub>	O*C <sub>10</sub> H <sub>12</sub> Li <sub>2</sub>
O*C <sub>6</sub> H <sub>11</sub> ClHg	O*C <sub>10</sub> H <sub>13</sub> Li
O*C <sub>6</sub> H <sub>12</sub> Br <sub>2</sub> Hg <sub>2</sub>	O*C <sub>10</sub> H <sub>13</sub> Li <sub>2</sub> N
O*C <sub>6</sub> H <sub>12</sub> Li <sub>2</sub>	O*C <sub>10</sub> H <sub>14</sub>
O*C <sub>6</sub> H <sub>13</sub> Na	O*C <sub>10</sub> H <sub>14</sub> LiN
O*C <sub>7</sub> H <sub>3</sub> ClF <sub>4</sub> Hg	O*C <sub>10</sub> H <sub>19</sub> K
O*C <sub>7</sub> H <sub>5</sub> HgN	O*C <sub>10</sub> H <sub>21</sub> Li
O*C <sub>7</sub> H <sub>6</sub> FLi	O*C <sub>11</sub> H <sub>11</sub> Li
O*C <sub>7</sub> H <sub>6</sub> Li <sub>2</sub>	O*C <sub>11</sub> H <sub>12</sub> LiN
O*C <sub>7</sub> H <sub>7</sub> BrHg	O*C <sub>11</sub> H <sub>13</sub> Li <sub>2</sub> N
O*C <sub>7</sub> H <sub>7</sub> Cu	O*C <sub>11</sub> H <sub>14</sub>
O*C <sub>7</sub> H <sub>7</sub> Li	O*C <sub>11</sub> H <sub>14</sub> LiN
O*C <sub>7</sub> H <sub>8</sub>	O*C <sub>11</sub> H <sub>14</sub> Li <sub>2</sub>
O*C <sub>7</sub> H <sub>13</sub> ClHg	O*C <sub>11</sub> H <sub>19</sub> LiN <sub>2</sub>
O*C <sub>7</sub> H <sub>13</sub> Li	O*C <sub>11</sub> H <sub>23</sub> ClHg

O*C <sub>12</sub> H <sub>8</sub>	OP*C <sub>15</sub> H <sub>16</sub> Li
O*C <sub>12</sub> H <sub>8</sub> ClLi	OP*C <sub>16</sub> H <sub>16</sub> Li
O*C <sub>12</sub> H <sub>8</sub> Li <sub>2</sub>	OP*C <sub>23</sub> H <sub>26</sub> FeLi
O*C <sub>12</sub> H <sub>9</sub> Li	OP*C <sub>54</sub> H <sub>45</sub> Au <sub>3</sub> BF <sub>4</sub>
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O*C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> Hg <sub>2</sub>	OPS*C <sub>19</sub> H <sub>16</sub> Li
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O*C <sub>12</sub> H <sub>15</sub> Li <sub>2</sub> N	OS*C <sub>2</sub> H <sub>5</sub> K
O*C <sub>13</sub> H <sub>9</sub> K	OS*C <sub>2</sub> H <sub>5</sub> Li
O*C <sub>13</sub> H <sub>10</sub>	OS*C <sub>2</sub> H <sub>5</sub> Na
O*C <sub>13</sub> H <sub>10</sub> Li <sub>2</sub>	OS*C <sub>3</sub> H <sub>8</sub> LiN
O*C <sub>13</sub> H <sub>12</sub> AsLi	OS*C <sub>4</sub> H <sub>7</sub> Li
O*C <sub>13</sub> H <sub>16</sub>	OS*C <sub>5</sub> H <sub>7</sub> Li
O*C <sub>13</sub> H <sub>16</sub> LiN	OS*C <sub>5</sub> H <sub>9</sub> Li
O*C <sub>13</sub> H <sub>16</sub> Li <sub>2</sub>	OS*C <sub>5</sub> H <sub>11</sub> Li
O*C <sub>13</sub> H <sub>18</sub> Li <sub>2</sub>	OS*C <sub>7</sub> H <sub>6</sub> ClLi
O*C <sub>14</sub> H <sub>10</sub> F <sub>4</sub> Hg	OS*C <sub>7</sub> H <sub>7</sub> Li
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O*C <sub>14</sub> H <sub>14</sub> AsLi	OS*C <sub>7</sub> H <sub>12</sub> LiN
O*C <sub>14</sub> H <sub>18</sub>	OS*C <sub>7</sub> H <sub>15</sub> GeLi
O*C <sub>15</sub> H <sub>10</sub> LiN	OS*C <sub>7</sub> H <sub>15</sub> Li
O*C <sub>15</sub> H <sub>11</sub> Cl <sub>3</sub> FHg <sub>2</sub>	OS*C <sub>7</sub> H <sub>16</sub> Ge
O*C <sub>15</sub> H <sub>12</sub> ClFHg	OS*C <sub>8</sub> H <sub>8</sub> LiN
O*C <sub>15</sub> H <sub>14</sub> Li <sub>2</sub>	OS*C <sub>8</sub> H <sub>9</sub> Li
O*C <sub>16</sub> H <sub>15</sub> ClHg	OS*C <sub>8</sub> H <sub>9</sub> Li <sub>2</sub> N
O*C <sub>18</sub> H <sub>28</sub> LiN	OS*C <sub>8</sub> H <sub>10</sub> LiN
O*C <sub>19</sub> H <sub>15</sub> Li	OS*C <sub>9</sub> H <sub>9</sub> Li
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O*C <sub>20</sub> H <sub>14</sub> Li <sub>2</sub>	OS*C <sub>10</sub> H <sub>11</sub> Li
O*C <sub>20</sub> H <sub>16</sub> Li <sub>2</sub>	OS*C <sub>10</sub> H <sub>12</sub>
O*C <sub>20</sub> H <sub>32</sub> LiN	OS*C <sub>10</sub> H <sub>14</sub>
O*C <sub>21</sub> H <sub>26</sub> Au	OS*C <sub>11</sub> H <sub>14</sub>
O*C <sub>21</sub> H <sub>22</sub> LiN	OS*C <sub>11</sub> H <sub>16</sub>
O*C <sub>28</sub> H <sub>21</sub> Au	OS*C <sub>14</sub> H <sub>19</sub> Li
O*Cd	OS*C <sub>16</sub> H <sub>18</sub>
O*Cu <sub>2</sub>	OS*C <sub>18</sub> H <sub>27</sub> Li
O*HK	OS*C <sub>21</sub> H <sub>17</sub> Li
O*HLi	OSSI*C <sub>7</sub> H <sub>15</sub> Li
O*HNa	OSSI*C <sub>7</sub> H <sub>16</sub>
O*Hg	OSSI*C <sub>10</sub> H <sub>15</sub> Li
OP*C <sub>5</sub> H <sub>13</sub> ClLiN <sub>2</sub>	OSSI*C <sub>15</sub> H <sub>24</sub>
OP*C <sub>5</sub> H <sub>14</sub> LiN <sub>2</sub>	OSSn*C <sub>7</sub> H <sub>16</sub>
OP*C <sub>6</sub> H <sub>17</sub> LiN <sub>3</sub>	OSSn*C <sub>17</sub> H <sub>36</sub>
OP*C <sub>7</sub> H <sub>16</sub> LiN <sub>2</sub>	OS <sub>2</sub> *C <sub>3</sub> H <sub>7</sub> Li
OP*C <sub>8</sub> H <sub>19</sub> LiN <sub>2</sub>	OS <sub>2</sub> *C <sub>4</sub> H <sub>7</sub> Li
OP*C <sub>10</sub> H <sub>24</sub> Cu	OS <sub>2</sub> *C <sub>4</sub> H <sub>9</sub> Li
OP*C <sub>12</sub> H <sub>14</sub> Li	OS <sub>2</sub> *C <sub>6</sub> H <sub>11</sub> Li
OP*C <sub>12</sub> H <sub>19</sub> LiN <sub>3</sub>	OS <sub>2</sub> *C <sub>7</sub> H <sub>12</sub> LiN
OP*C <sub>12</sub> H <sub>21</sub> LiN <sub>3</sub>	OS <sub>2</sub> *C <sub>8</sub> H <sub>15</sub> Li
OP*C <sub>13</sub> H <sub>12</sub> Li	OS <sub>2</sub> *C <sub>9</sub> H <sub>15</sub> Li
OP*C <sub>14</sub> H <sub>14</sub> Li	OS <sub>2</sub> *C <sub>12</sub> H <sub>13</sub> Li

- $\text{OS}_2^*\text{C}_{13}\text{H}_{15}\text{Li}$   
 $\text{OS}_2^*\text{C}_{18}\text{H}_{22}$   
 $\text{OSe}^*\text{C}_7\text{H}_7\text{Li}$   
 $\text{OSe}^*\text{C}_6\text{H}_9\text{Li}$   
 $\text{OSe}^*\text{C}_9\text{H}_8\text{F}_3\text{Li}$   
 $\text{OSe}^*\text{C}_9\text{H}_{11}\text{Li}$   
 $\text{OSe}^*\text{C}_{11}\text{H}_{11}\text{Li}$   
 $\text{OSe}^*\text{C}_{13}\text{H}_{11}\text{Li}$   
 $\text{OSe}^*\text{C}_{14}\text{H}_{11}\text{Li}$   
 $\text{OSe}^*\text{C}_{14}\text{H}_{13}\text{Li}$   
 $\text{OSe}^*\text{C}_{14}\text{H}_{17}\text{Li}$   
 $\text{OSe}^*\text{C}_{15}\text{H}_{15}\text{Li}$   
 $\text{OSe}^*\text{C}_{17}\text{H}_{27}\text{Li}$   
 $\text{OSe}_2^*\text{C}_{14}\text{H}_{14}$   
 $\text{OSi}^*\text{C}_3\text{H}_9\text{Na}$   
 $\text{OSi}^*\text{C}_4\text{H}_{11}\text{Li}$   
 $\text{OSi}^*\text{C}_4\text{H}_{12}$   
 $\text{OSi}^*\text{C}_5\text{H}_{11}\text{Li}$   
 $\text{OSi}^*\text{C}_5\text{H}_{13}\text{Li}$   
 $\text{OSi}^*\text{C}_6\text{H}_{13}\text{Li}$   
 $\text{OSi}^*\text{C}_7\text{H}_{14}\text{LiN}$   
 $\text{OSi}^*\text{C}_7\text{H}_{15}\text{Li}$   
 $\text{OSi}^*\text{C}_7\text{H}_{16}\text{LiN}$   
 $\text{OSi}^*\text{C}_7\text{H}_{17}\text{Li}$   
 $\text{OSi}^*\text{C}_8\text{H}_{14}\text{LiN}$   
 $\text{OSi}^*\text{C}_9\text{H}_{19}\text{Li}$   
 $\text{OSi}^*\text{C}_{11}\text{H}_{14}\text{LiN}$   
 $\text{OSi}^*\text{C}_{11}\text{H}_{23}\text{Li}$   
 $\text{OSi}^*\text{C}_{12}\text{H}_{21}\text{Li}$   
 $\text{OSi}^*\text{C}_{12}\text{H}_{25}\text{Li}$   
 $\text{OSi}^*\text{C}_{20}\text{H}_{17}\text{Li}$   
 $\text{OSiSn}^*\text{C}_7\text{H}_{20}$   
 $\text{OSiSn}^*\text{C}_{23}\text{H}_{50}$   
 $\text{OSiSn}^*\text{C}_{24}\text{H}_{48}$   
 $\text{OSiSn}^*\text{C}_{24}\text{H}_{52}$   
 $\text{OSi}_6\text{Sn}_2^*\text{C}_{24}\text{H}_{66}$   
 $\text{OSn}^*\text{C}_4\text{H}_{12}$   
 $\text{OSn}^*\text{C}_{14}\text{H}_{32}$   
 $\text{OSn}^*\text{C}_{15}\text{H}_{34}$   
 $\text{OSn}^*\text{C}_{16}\text{H}_{37}\text{N}$   
 $\text{OSn}^*\text{C}_{17}\text{H}_{38}\text{Li}_2$   
 $\text{OSn}^*\text{C}_{18}\text{H}_{36}$   
 $\text{OSn}^*\text{C}_{20}\text{H}_{44}$   
 $\text{OSn}^*\text{C}_{21}\text{H}_{20}$   
 $\text{OSn}^*\text{C}_{21}\text{H}_{44}$   
 $\text{OSn}^*\text{C}_{22}\text{H}_{22}$   
 $\text{OZn}^*\text{CH}_3\text{Cl}$   
 $\text{OZn}^*\text{C}_5\text{H}_{10}$   
 $\text{OZn}^*\text{C}_6\text{H}_{12}\text{BrN}$   
 $\text{OZn}^*\text{C}_{10}\text{H}_{12}$   
 $\text{O}_2^*\text{C}_2\text{Cl}_2\text{Li}_2$   
 $\text{O}_2^*\text{C}_2\text{H}_4\text{Li}_2\text{N}$   
 $\text{O}_2^*\text{C}_2\text{H}_5\text{ClHg}$   
 $\text{O}_2^*\text{C}_2\text{HgN}_2$   
 $\text{O}_2^*\text{C}_3\text{H}_2\text{CuN}$   
 $\text{O}_2^*\text{C}_3\text{H}_4\text{Li}_2$   
 $\text{O}_2^*\text{C}_3\text{H}_4\text{Li}_2\text{N}$   
 $\text{O}_2^*\text{C}_3\text{H}_7\text{ClHg}$   
 $\text{O}_2^*\text{C}_3\text{H}_8\text{BClHg}$   
 $\text{O}_2^*\text{C}_3\text{Li}_2$   
 $\text{O}_2^*\text{C}_4\text{H}_2\text{Li}_2$   
 $\text{O}_2^*\text{C}_4\text{H}_4\text{Li}_2$   
 $\text{O}_2^*\text{C}_4\text{H}_5\text{Cl}_2\text{Li}$   
 $\text{O}_2^*\text{C}_4\text{H}_5\text{Cl}_3\text{Hg}$   
 $\text{O}_2^*\text{C}_4\text{H}_5\text{HgN}$   
 $\text{O}_2^*\text{C}_4\text{H}_5\text{LiN}_2$   
 $\text{O}_2^*\text{C}_4\text{H}_6$   
 $\text{O}_2^*\text{C}_4\text{H}_6\text{Hg}$   
 $\text{O}_2^*\text{C}_4\text{H}_6\text{HgN}_2$   
 $\text{O}_2^*\text{C}_4\text{H}_6\text{LiN}$   
 $\text{O}_2^*\text{C}_4\text{H}_6\text{Li}_2$   
 $\text{O}_2^*\text{C}_4\text{H}_7\text{Li}$   
 $\text{O}_2^*\text{C}_4\text{H}_8$   
 $\text{O}_2^*\text{C}_4\text{H}_8\text{Cl}_2\text{Hg}_2$   
 $\text{O}_2^*\text{C}_5\text{H}_3\text{F}_6\text{HgN}$   
 $\text{O}_2^*\text{C}_5\text{H}_6\text{Hg}$   
 $\text{O}_2^*\text{C}_5\text{H}_6\text{Li}_2$   
 $\text{O}_2^*\text{C}_5\text{H}_7\text{ClHg}$   
 $\text{O}_2^*\text{C}_5\text{H}_8\text{ClNa}$   
 $\text{O}_2^*\text{C}_5\text{H}_8\text{Hg}$   
 $\text{O}_2^*\text{C}_5\text{H}_9\text{BrHg}$   
 $\text{O}_2^*\text{C}_5\text{H}_9\text{Li}$   
 $\text{O}_2^*\text{C}_5\text{H}_{11}\text{Li}$   
 $\text{O}_2^*\text{C}_6\text{H}_4\text{BrHgN}$   
 $\text{O}_2^*\text{C}_6\text{H}_4\text{ClHgN}$   
 $\text{O}_2^*\text{C}_6\text{H}_4\text{HgIN}$   
 $\text{O}_2^*\text{C}_6\text{H}_4\text{LiN}$   
 $\text{O}_2^*\text{C}_6\text{H}_5\text{BrF}_6\text{Hg}$   
 $\text{O}_2^*\text{C}_6\text{H}_5\text{LiN}$   
 $\text{O}_2^*\text{C}_6\text{H}_5\text{N}$   
 $\text{O}_2^*\text{C}_6\text{H}_7\text{B}$   
 $\text{O}_2^*\text{C}_6\text{H}_8\text{ClLi}$   
 $\text{O}_2^*\text{C}_6\text{H}_{10}\text{ClHgN}$   
 $\text{O}_2^*\text{C}_6\text{H}_{10}\text{Hg}$   
 $\text{O}_2^*\text{C}_6\text{H}_{10}\text{Li}_2$   
 $\text{O}_2^*\text{C}_6\text{H}_{11}\text{Li}$   
 $\text{O}_2^*\text{C}_6\text{H}_{12}\text{Cl}_2\text{Hg}_2$   
 $\text{O}_2^*\text{C}_6\text{H}_{12}\text{LiN}$   
 $\text{O}_2^*\text{C}_6\text{H}_{13}\text{Li}$   
 $\text{O}_2^*\text{C}_7\text{H}_4\text{Li}_2$   
 $\text{O}_2^*\text{C}_7\text{H}_6\text{LiN}$   
 $\text{O}_2^*\text{C}_7\text{H}_{11}\text{Li}$   
 $\text{O}_2^*\text{C}_7\text{H}_{12}\text{Hg}$   
 $\text{O}_2^*\text{C}_7\text{H}_{15}\text{BrHg}$

$O_2^*C_7H_{15}Li$	$O_2^*C_{12}H_{17}Li$
$O_2^*C_8F_8Hg$	$O_2^*C_{12}H_{18}Hg$
$O_2^*C_8H_3F_5Hg$	$O_2^*C_{12}H_{18}HgN_4$
$O_2^*C_8H_5F_3Hg$	$O_2^*C_{12}H_{22}$
$O_2^*C_8H_6Cl_2Hg$	$O_2^*C_{13}H_5Br_5Hg$
$O_2^*C_8H_6Li_2$	$O_2^*C_{13}H_5Cl_5Hg$
$O_2^*C_8H_7BrHg$	$O_2^*C_{13}H_5F_5Hg$
$O_2^*C_8H_7ClHg$	$O_2^*C_{14}H_6Br_8Hg$
$O_2^*C_8H_8Hg$	$O_2^*C_{14}H_6F_8Hg$
$O_2^*C_8H_9BrHg$	$O_2^*C_{14}H_7Cl_5Hg$
$O_2^*C_8H_9BrMg$	$O_2^*C_{14}H_{14}Hg$
$O_2^*C_8H_9ClHg$	$O_2^*C_{15}H_{10}Li_2$
$O_2^*C_8H_9Li$	$O_2^*C_{15}H_{11}K$
$O_2^*C_8H_{11}B$	$O_2^*C_{15}H_{14}Fe$
$O_2^*C_8H_{11}Li$	$O_2^*C_{16}H_{12}Li_2$
$O_2^*C_8H_{12}Li_2$	$O_2^*C_{16}H_{14}Hg$
$O_2^*C_8H_{13}ClHg$	$O_2^*C_{16}H_{15}ClHg$
$O_2^*C_8H_{13}Li$	$O_2^*C_{16}H_{16}Cl_2Hg_2$
$O_2^*C_8H_{14}Hg$	$O_2^*C_{16}H_{24}Hg$
$O_2^*C_9H_6Li_2$	$O_2^*C_{16}H_{27}B$
$O_2^*C_9H_8Li_2$	$O_2^*C_{17}H_{25}Li$
$O_2^*C_9H_9ClHg$	$O_2^*C_{18}H_{14}Hg$
$O_2^*C_9H_9Li$	$O_2^*C_{18}H_{18}Hg$
$O_2^*C_9H_{11}ClHg$	$O_2^*C_{18}H_{27}Li$
$O_2^*C_9H_{11}HgN$	$O_2^*C_{20}H_{24}HgN_2$
$O_2^*C_9H_{11}Li$	$O_2^*C_{20}H_{33}HgN$
$O_2^*C_9H_{12}LiN$	$O_2^*C_{22}H_{22}Hg$
$O_2^*C_9H_{13}B$	$O_2^*C_{38}H_{30}$
$O_2^*C_9H_{14}LiN$	$O_2P^*C_7H_{16}LiN_2$
$O_2^*C_9H_{16}Hg$	$O_2P^*C_8H_{14}Li$
$O_2^*C_9H_{17}Li$	$O_2P^*C_{17}H_{19}LiN$
$O_2^*C_{10}H_6F_4Hg_2$	$O_2P^*C_{23}H_{21}AuN$
$O_2^*C_{10}H_{10}BClFe$	$O_2P^*C_{25}H_{15}AuF_5$
$O_2^*C_{10}H_{11}BFe$	$O_2PS^*C_3H_8Li$
$O_2^*C_{10}H_{12}BrLi$	$O_2PS^*C_5H_{11}ClLi$
$O_2^*C_{10}H_{12}Hg$	$O_2P_2^*C_{10}H_{20}CdF_4$
$O_2^*C_{10}H_{14}Cu$	$O_2P_2^*C_{25}H_{21}BrHg$
$O_2^*C_{10}H_{18}Hg$	$O_2P_2^*C_{25}H_{21}Li$
$O_2^*C_{10}H_{21}Li$	$O_2P_2^*C_{26}H_{20}HgN_4$
$O_2^*C_{11}H_{11}Li$	$O_2P_2^*C_{40}H_{35}Cu$
$O_2^*C_{11}H_{13}Li$	$O_2Pb^*C_{20}H_{18}$
$O_2^*C_{11}H_{13}Li_2N$	$O_2S^*C_2H_4Li$
$O_2^*C_{11}H_{14}Hg$	$O_2S^*C_3H_7Li_2N$
$O_2^*C_{11}H_{15}Li$	$O_2S^*C_3H_8LiN$
$O_2^*C_{11}H_{18}Cl_2Hg_2$	$O_2S^*C_4H_5B$
$O_2^*C_{11}H_{19}ClHg$	$O_2S^*C_4H_6$
$O_2^*C_{11}H_{21}Li$	$O_2S^*C_5H_{10}LiN$
$O_2^*C_{11}H_{23}Li$	$O_2S^*C_6H_4Cl_2Hg$
$O_2^*C_{12}H_{10}Hg$	$O_2S^*C_6H_6ClHgN$
$O_2^*C_{12}H_{14}LiN$	$O_2S^*C_6H_9Li$
$O_2^*C_{12}H_{15}Li$	$O_2S^*C_6H_{11}ClHg$
$O_2^*C_{12}H_{16}LiN$	$O_2S^*C_6H_{11}Li$

$O_2S^*C_6H_{13}ClHg$	$O_2Zn^*C_{44}H_{20}F_{30}Ge_2$
$O_2S^*C_7H_5Li_3$	$O_3^*AgN$
$O_2S^*C_7H_6Li_2$	$O_3^*CH_3Ag_2N$
$O_2S^*C_7H_7ClHg$	$O_3^*CK_2$
$O_2S^*C_7H_7Li$	$O_3^*CNa_2$
$O_2S^*C_8H_6Li_2$	$O_3^*C_3H_9CrN_3$
$O_2S^*C_8H_{10}Hg$	$O_3^*C_4H_5B$
$O_2S^*C_8H_{10}LiN$	$O_3^*C_5H_2Li_2$
$O_2S^*C_8H_{16}Li_2$	$O_3^*C_5H_8D_2Hg$
$O_2S^*C_9H_7Li_2N$	$O_3^*C_5H_{10}LiN$
$O_2S^*C_9H_9Li$	$O_3^*C_6H_5HgN$
$O_2S^*C_{10}H_{11}BrHg_2$	$O_3^*C_7H_{12}Hg$
$O_2S^*C_{10}H_{11}Li$	$O_3^*C_8H_4AgMn$
$O_2S^*C_{11}H_{13}Li$	$O_3^*C_8H_4BrHgMn$
$O_2S^*C_{11}H_{13}Li_2N_2$	$O_3^*C_8H_4ClHgMn$
$O_2S^*C_{11}H_{19}Li$	$O_3^*C_8H_4CuMn$
$O_2S^*C_{12}H_8BrLi$	$O_3^*C_8H_6ClHgN$
$O_2S^*C_{12}H_8Cl_2Hg$	$O_3^*C_8H_6Li_2$
$O_2S^*C_{12}H_8Li_2$	$O_3^*C_8H_8Hg$
$O_2S^*C_{12}H_9Li$	$O_3^*C_8H_9Hg_3N$
$O_2S^*C_{12}H_{10}Hg$	$O_3^*C_8H_{13}ClHg$
$O_2S^*C_{12}H_{13}ClHg$	$O_3^*C_8H_{14}$
$O_2S^*C_{12}H_{14}LiN$	$O_3^*C_8H_{14}Hg$
$O_2S^*C_{13}H_{12}Hg$	$O_3^*C_9H_5ClCrHg$
$O_2S^*C_{16}H_{18}LiN$	$O_3^*C_9H_5CrLi$
$O_2S^*C_{17}H_{14}Li_2$	$O_3^*C_9H_6Cr$
$O_2S^*C_{21}H_{17}Li$	$O_3^*C_9H_9Li$
$O_2Se^*C_8H_6Li_2$	$O_3^*C_9H_{10}Hg$
$O_2Se^*C_9H_9Li$	$O_3^*C_9H_{13}Li$
$O_2Se^*C_9H_{13}Li$	$O_3^*C_9H_{15}F_3Hg$
$O_2Se^*C_{11}H_{11}Li$	$O_3^*C_9H_{15}Li$
$O_2Si^*C_3H_9Na$	$O_3^*C_9H_{18}Hg$
$O_2Si^*C_5H_{10}Li_2$	$O_3^*C_{10}H_{11}HgN$
$O_2Si^*C_7H_{12}Hg$	$O_3^*C_{11}H_{11}LiMnN$
$O_2Si^*C_7H_{15}Li$	$O_3^*C_{12}H_{17}Li$
$O_2Si^*C_9H_{18}ClLi$	$O_3^*C_{14}H_{20}LiN$
$O_2Si^*C_9H_{19}Li$	$O_3^*C_{14}H_{26}ClHgN$
$O_2Si^*C_{10}H_{22}BLi$	$O_3^*C_{15}H_{10}F_4Hg$
$O_2Si_2^*C_6H_{18}$	$O_3^*C_{15}H_{20}LiN$
$O_2Si_2^*C_{12}H_{27}Li$	$O_3^*C_{18}H_{20}Hg$
$O_2Sn^*C_{17}H_{38}$	$O_3^*C_{21}H_{22}Ge$
$O_2Sn^*C_{18}H_{40}$	$O_3^*C_{24}H_{27}Bi$
$O_2Sn^*C_{20}H_{40}$	$O_3^*C_{30}H_{36}Ag_3N_3$
$O_2Sn^*C_{22}H_{48}$	$O_3^*C_{30}H_{36}Au_3N_3$
$O_2Sn^*C_{23}H_{42}$	$O_3^*C_{33}H_{36}Ag_3N_3$
$O_2Sn^*C_{23}H_{48}$	$O_3P^*C_3H_8Li$
$O_2Sn^*C_{23}H_{50}$	$O_3P^*C_5H_{10}BrCdF_2$
$O_2Sn^*C_{24}H_{44}$	$O_3P^*C_5H_{10}Cl_2Li$
$O_2Sn^*C_{30}H_{54}$	$O_3P^*C_5H_{11}ClLi$
$O_2Ti^*C_4H_7$	$O_3P^*C_6H_{11}LiN$
$O_2Zn^*C_2H_6$	$O_3P^*C_8H_{15}LiN$
$O_2Zn^*C_{10}H_{22}$	$O_3P^*C_8H_{16}Li$

$O_3P^*C_9H_{19}LiN$	$O_4^*C_{12}F_8HgN_2$
$O_3PS^*C_6H_{14}Li$	$O_4^*C_{12}H_8HgN_2$
$O_3Pb^*C_{21}H_{21}Na$	$O_4^*C_{13}H_{22}Hg$
$O_3Pb^*C_{24}H_{27}Na$	$O_4^*C_{14}Br_8Cl_2Hg$
$O_3Re^*C_8H_4BrHg$	$O_4^*C_{14}Br_8F_2Hg$
$O_3Re^*C_8H_4ClHg$	$O_4^*C_{14}Cl_{10}Hg$
$O_3Re^*C_8H_4Li$	$O_4^*C_{14}F_{10}Hg$
$O_3S^*CAgF_3$	$O_4^*C_{14}H_6F_4Hg$
$O_3S^*CCuF_3$	$O_4^*C_{14}H_{10}Li_2$
$O_3S^*C_2H_5Li$	$O_4^*C_{16}H_{14}Hg$
$O_3S^*C_4H_7Li$	$O_4^*C_{17}H_{16}Hg$
$O_3S^*C_5H_9Li$	$O_4^*C_{20}H_{20}F_{14}Hg$
$O_3S^*C_6H_4Li_2$	$O_4^*C_{22}H_{38}Hg$
$O_3S^*C_6H_7Li$	$O_4P^*C_3H_3Hg_3$
$O_3S^*C_8H_9Li$	$O_4P^*C_6H_{12}Li$
$O_3S^*C_9H_8Li_2$	$O_4P^*C_6H_{15}Hg_3$
$O_3S^*C_9H_{10}LiN$	$O_4P^*C_7H_{14}Li$
$O_3S^*C_{12}H_2F_8Hg$	$O_4P^*C_{26}H_{26}Li$
$O_3S^*C_{15}H_{13}Li$	$O_4P_2^*C_{42}H_{35}CuN_2$
$O_3S_2^*C_9H_{12}LiN$	$O_4S^*C_4H_{10}$
$O_3S_2^*C_{14}H_{14}LiN$	$O_4S^*C_{21}H_{15}CrLi$
$O_3Si^*C_{12}H_{24}$	$O_4S^*C_{21}H_{15}LiMo$
$O_3Si_4^*C_{21}H_{51}Li$	$O_4S^*Na_2$
$O_3Sn^*C_{21}H_{40}$	$O_4SW^*C_{21}H_{15}Li$
$O_3Sn^*C_{24}H_{44}$	$O_4SZn^*C_4H_{10}$
$O_3Zn^*C_{26}H_{34}Ge$	$O_4S_2^*C_{12}H_8F_2Hg$
$O_3Zn^*C_{42}H_{44}Ge_2$	$O_4S_2^*C_{12}H_{10}Hg$
$O_4^*C_4F_6Hg$	$O_4S_2^*C_{14}H_{14}Hg$
$O_4^*C_4H_3Li_3$	$O_4Si^*C_{18}H_{25}CrLi$
$O_4^*C_4H_6Hg$	$O_4Si_2^*C_6H_{18}$
$O_4^*C_5H_9Li$	$O_4Si_2^*C_9H_{19}Li$
$O_4^*C_6H_{10}Hg$	$O_4Sn^*C_8H_{20}$
$O_4^*C_6H_{15}AsHg_3$	$O_4Sn^*C_{12}H_{28}$
$O_4^*C_7H_{12}Hg$	$O_4Sn^*C_{16}H_{36}$
$O_4^*C_7H_{13}B_2Li$	$O_4Sn^*C_{32}H_{36}$
$O_4^*C_8F_4Hg$	$O_4Zn^*C_8H_{10}N_4$
$O_4^*C_8H_7HgN$	$O_4Zn^*C_{14}H_{10}$
$O_4^*C_8H_{10}CdN_4$	$O_4Zn^*C_{16}H_{14}$
$O_4^*C_8H_{10}Cl_4Hg_3$	$O_5^*C_3H_7ClHg$
$O_4^*C_8H_{10}HgN_4$	$O_5^*C_8H_6BMn$
$O_4^*C_8H_{12}Hg$	$O_5^*C_8H_8BN$
$O_4^*C_8H_{14}HgN_2$	$O_5^*C_8H_{11}Li$
$O_4^*C_9H_{11}Hg_2$	$O_5^*C_9H_7BCr$
$O_4^*C_9H_{16}HgN$	$O_5^*C_{15}H_9ClFeHgMn$
$O_4^*C_{10}F_{18}Hg$	$O_5^*C_{15}H_{10}FeMn$
$O_4^*C_{10}H_{10}Hg_2$	$O_5P^*C_7H_{14}Li$
$O_4^*C_{10}H_{11}Hg_2N$	$O_5P^*C_8H_{18}Li$
$O_4^*C_{10}H_{12}Li_2$	$O_5P^*C_{10}H_{20}Li$
$O_4^*C_{10}H_{14}Hg$	$O_5P^*C_{16}H_{15}Li_2$
$O_4^*C_{10}H_{15}Li$	$O_5PS^*C_6H_{14}Li$
$O_4^*C_{11}H_{23}HgN$	$O_5Re^*C_8H_6B$
$O_4^*C_{12}Cl_8HgN_2$	$O_5SSi^*C_{24}H_{35}Li$



$O_6^*C_3H_6ClHgN$	$P^*C_6H_{12}LiO_4$
$O_6^*C_{10}H_{18}B_3Li$	$P^*C_6H_{15}Hg_3O_4$
$O_6^*C_{12}H_{18}Cd$	$P^*C_6H_{17}LiN_3O$
$O_6^*C_{12}H_{18}Hg$	$P^*C_6H_{18}Au$
$O_6^*C_{15}H_{20}Hg_2$	$P^*C_7H_{14}LiO_4$
$O_6^*C_{16}H_6Br_8Hg$	$P^*C_7H_{14}LiO_5$
$O_6^*C_{16}H_8AgCuMn$	$P^*C_7H_{16}LiN_2O$
$O_6^*C_{18}H_{10}Cr_2Hg$	$P^*C_7H_{16}LiN_2O_2$
$O_6^*HgN_2$	$P^*C_8H_{14}LiO_2$
$O_6P_2^*C_9H_{20}ClLi$	$P^*C_8H_{15}LiNO_3$
$O_6S_2^*C_{15}H_{14}Hg$	$P^*C_8H_{16}LiO_3$
$O_6S_2^*C_{18}H_2Cl_{12}Hg_2$	$P^*C_8H_{18}Li$
$O_6S_2^*C_{18}H_2F_{12}Hg_2$	$P^*C_8H_{18}LiO_5$
$O_6S_2^*C_{22}H_{10}F_{10}HgN_2$	$P^*C_8H_{19}LiN_2O$
$O_6S_2^*C_{22}H_{10}HgN_2$	$P^*C_9H_{19}LiNO_3$
$O_6S_2^*C_{22}H_{12}Cl_8HgN_2$	$P^*C_9H_{20}Li$
$O_6S_2^*C_{22}H_{12}F_8HgN_2$	$P^*C_{10}H_{20}LiO_5$
$O_6S_2^*C_{34}H_{40}Ag_4Au_2F_6N_4$	$P^*C_{10}H_{24}CuO$
$O_6Si_3^*C_{21}H_5^7HgLi$	$P^*C_{11}H_{20}Cu$
$O_7^*C_{10}H_{21}HgN_2$	$P^*C_{12}H_{10}Li$
$O_8^*C_2F_2HgN_4$	$P^*C_{12}H_{14}LiO$
$O_8^*C_{10}H_{14}Hg$	$P^*C_{12}H_{19}LiN_3O$
$O_8^*C_{13}H_{24}B_4$	$P^*C_{12}H_{21}Hg_2O_9$
$O_8^*C_{14}H_8HgN_2$	$P^*C_{12}H_{21}LiN_3O$
$O_8^*C_{14}H_{22}Hg$	$P^*C_{13}H_{12}Li$
$O_8S_2^*C_{12}H_4Cl_{10}Hg$	$P^*C_{13}H_{12}LiO$
$O_8S_2^*C_{12}H_4F_{10}Hg$	$P^*C_{14}H_{14}LiO$
$O_8S_2^*C_{12}H_6Cl_8Hg$	$P^*C_{15}H_{16}LiO$
$O_8S_2^*C_{12}H_6F_8Hg$	$P^*C_{16}H_{15}Li_2O_5$
$O_8S_2^*C_{17}H_{16}Hg_2$	$P^*C_{16}H_{16}LiO$
$O_8Si_4^*C_{28}H_7HgLi_2$	$P^*C_{17}H_{19}LiNO_2$
$O_9P^*C_{12}H_{21}Hg_2$	$P^*C_{18}H_{15}$
$O_{10}^*C_{16}HF_{15}Hg_5$	$P^*C_{18}H_{15}AuCl$
$O_{10}^*C_{17}H_3F_{15}Hg_5$	$P^*C_{18}H_{15}BrCu$
$O_{10}P_2^*C_{13}H_{26}Hg_2$	$P^*C_{18}H_{20}Au$
$O_{12}^*C_2HgN_6$	$P^*C_{18}H_{22}Li$
$O_{12}^*C_4H_4HgN_6$	$P^*C_{19}H_{16}BrHg$
$O_{12}^*C_{12}H_4HgN_6$	$P^*C_{19}H_{16}Br_2CuHg$
$O_{12}^*C_{16}F_{15}Hg_5N$	$P^*C_{19}H_{16}Li$
$O_{12}^*C_{18}F_{18}Hg_6$	$P^*C_{19}H_{18}Au$
$O_{16}^*C_{14}H_4HgN_6$	$P^*C_{20}H_{20}Au$
$O_{16}^*C_{26}F_{24}Hg_8$	$P^*C_{20}H_{32}CuN$
$P^*C_3H_8Li$	$P^*C_{21}H_{24}AuGe$
$P^*C_3H_8LiO_3$	$P^*C_{23}H_{20}Ag$
$P^*C_3H_9Hg_3O_4$	$P^*C_{23}H_{20}Au$
$P^*C_4H_{11}$	$P^*C_{23}H_{20}Cu$
$P^*C_5H_{10}BrCdF_2O_3$	$P^*C_{23}H_{20}FeLiO$
$P^*C_5H_{10}Cl_2LiO_3$	$P^*C_{23}H_{21}AuNO_2$
$P^*C_5H_{11}ClLiO_3$	$P^*C_{24}H_{15}AuF_5$
$P^*C_5H_{13}ClLiN_2O$	$P^*C_{24}H_{20}Au$
$P^*C_5H_{14}LiN_2O$	$P^*C_{25}H_{15}AuF_5O_2$
$P^*C_6H_{11}LiNO_3$	$P^*C_{25}H_{22}Au$

$P^*C_{26}H_{22}Au$   
 $P^*C_{26}H_{26}LiO_4$   
 $P^*C_{27}H_{27}AuN$   
 $P^*C_{30}H_{15}AuClF_{10}$   
 $P^*C_{36}H_{30}AuGe$   
 $P^*C_{42}H_{30}AuF_5$   
 $P^*C_{54}H_{45}Au_3BF_4O$   
 $PS^*C_3H_8LiO_2$   
 $PS^*C_5H_{11}ClLiO_2$   
 $PS^*C_6H_{14}LiO_3$   
 $PS^*C_6H_{14}LiO_5$   
 $PS^*C_8H_{10}Li$   
 $PS^*C_8H_{14}LiO$   
 $PS^*C_{12}H_{14}Li$   
 $PS^*C_{13}H_{18}Li$   
 $PS^*C_{19}H_{16}LiO$   
 $PS^*C_{23}H_{20}FeLi$   
 $PSi^*C_{36}H_{30}Au$   
 $PSi_2^*C_{19}H_{28}Li$   
 $PSn^*C_{18}H_{15}AuCl_3$   
 $P_2^*C_5H_{13}Li$   
 $P_2^*C_6H_{16}LiN$   
 $P_2^*C_6H_{18}BLi$   
 $P_2^*C_8H_{20}Cu_2$   
 $P_2^*C_9H_{20}ClLiO_6$   
 $P_2^*C_{10}H_{20}CdF_4O_2$   
 $P_2^*C_{10}H_{28}AuBr$   
 $P_2^*C_{13}H_{26}Hg_2O_{10}$   
 $P_2^*C_{25}H_{21}BrHgO_2$   
 $P_2^*C_{25}H_{21}Li$   
 $P_2^*C_{25}H_{21}LiO_2$   
 $P_2^*C_{25}H_{22}$   
 $P_2^*C_{26}H_{20}HgN_4O_2$   
 $P_2^*C_{28}H_{24}AuI$   
 $P_2^*C_{37}H_{33}Cu$   
 $P_2^*C_{38}H_{32}CuN$   
 $P_2^*C_{38}H_{35}Cu$   
 $P_2^*C_{39}H_{37}Cu$   
 $P_2^*C_{40}H_{30}Au_2F_6$   
 $P_2^*C_{40}H_{35}CuO_2$   
 $P_2^*C_{40}H_{39}Cu$   
 $P_2^*C_{42}H_{35}CuN_2O_4$   
 $P_2^*C_{43}H_{37}AuBF_4$   
 $P_2^*C_{44}H_{39}AuGe$   
 $P_2^*C_{72}H_{30}CdF_{30}Ge_2$   
 $P_2PbPt^*C_{60}H_{50}$   
 $P_2Pb_2Pt^*C_{72}H_{60}$   
 $P_2Pd^*C_{72}H_{60}CdGe_2$   
 $P_2Pd^*C_{72}H_{60}Ge_2Hg$   
 $P_2PtSn_2^*C_{78}H_{36}F_{30}Hg$   
 $P_2Si_2^*C_{17}H_{38}AgCl$   
 $P_2Sn^*C_{36}H_{30}AuCl_3$

$P_2Sn^*C_{36}H_{30}Au_2I_2$   
 $P_3^*C_7H_{18}Li$   
 $P_3^*C_{54}H_{45}AgCl$   
 $P_3^*C_{54}H_{45}AuCl$   
 $P_3^*C_{54}H_{45}ClCu$   
 $P_3^*C_{72}H_{60}CuGe$   
 $P_3Pd^*C_{54}H_{45}$   
 $P_3Sn^*C_{54}H_{45}AgCl_3$   
 $P_3Sn^*C_{54}H_{45}AuCl_3$   
 $P_3Sn^*C_{54}H_{45}Cl_3Cu$   
 $P_4^*C_{48}H_{108}Cu_4I_4$   
 $P_4^*C_{72}H_{60}Ag_4I_4$   
 $P_4^*C_{72}H_{60}Cu_4I_4$   
 $P_4Sn^*C_{72}H_{60}Au_4Cl_3$   
 $P_6^*C_{50}H_{72}Cu_2$   
 $P_6^*C_{52}H_{76}Cu_2$   
 $P_6^*C_{54}H_{80}Cu_2$   
 $P_6^*C_{54}H_{84}Cu_2$   
 $P_6^*C_{75}H_{63}Cu_3$   
**Pb**

Pb

Cathode: 5.5.7.1.3

Reaction with NaH: 5.5.7.1.2

$Pb^*Au_2$   
 $Pb^*Br_2$   
 $Pb^*C_2H_6Cl_2$   
 $Pb^*C_3H_9Br$   
 $Pb^*C_3H_9Cl$   
 $Pb^*C_3H_9K$   
 $Pb^*C_3H_9Li$   
 $Pb^*C_3H_9Na$   
 $Pb^*C_4H_{12}$   
 $Pb^*C_6H_9Na$   
 $Pb^*C_6H_{15}Li$   
 $Pb^*C_6H_{15}Na$   
 $Pb^*C_8H_{12}$   
 $Pb^*C_8H_{20}$   
 $Pb^*C_{10}H_{15}Na$   
 $Pb^*C_{12}H_{10}$   
 $Pb^*C_{12}H_{10}Cl_2$   
 $Pb^*C_{12}H_{10}Li_2$   
 $Pb^*C_{12}H_{20}$   
 $Pb^*C_{14}H_{22}$   
 $Pb^*C_{16}H_{20}$   
 $Pb^*C_{18}F_{15}Li$   
 $Pb^*C_{18}H_{15}Cl$   
 $Pb^*C_{18}H_{15}ClHg$   
 $Pb^*C_{18}H_{15}K$   
 $Pb^*C_{18}H_{15}Li$   
 $Pb^*C_{18}H_{15}Na$   
 $Pb^*C_{18}H_{33}Na$   
 $Pb^*C_{19}H_{15}Cl_2Li$

$\text{Pb}^*\text{C}_{19}\text{H}_{17}\text{Li}$   
 $\text{Pb}^*\text{C}_{20}\text{H}_{18}$   
 $\text{Pb}^*\text{C}_{20}\text{H}_{18}\text{O}_2$   
 $\text{Pb}^*\text{C}_{21}\text{H}_{18}\text{Cl}_2$   
 $\text{Pb}^*\text{C}_{21}\text{H}_{19}\text{Cl}$   
 $\text{Pb}^*\text{C}_{21}\text{H}_{21}\text{Cl}$   
 $\text{Pb}^*\text{C}_{21}\text{H}_{21}\text{Li}$   
 $\text{Pb}^*\text{C}_{21}\text{H}_{21}\text{Na}$   
 $\text{Pb}^*\text{C}_{21}\text{H}_{21}\text{NaO}_3$   
 $\text{Pb}^*\text{C}_{22}\text{H}_{21}\text{Cl}$   
 $\text{Pb}^*\text{C}_{24}\text{H}_{20}$   
 $\text{Pb}^*\text{C}_{24}\text{H}_{27}\text{NaO}_3$   
 $\text{Pb}^*\text{C}_{25}\text{H}_{20}\text{Cl}_2\text{Hg}$   
 $\text{Pb}^*\text{C}_{28}\text{H}_{28}$   
 $\text{Pb}^*\text{C}_{31}\text{H}_{26}\text{AsLi}$   
 $\text{Pb}^*\text{C}_{37}\text{H}_{30}\text{Cl}_2\text{Ge}$   
 $\text{Pb}^*\text{C}_{37}\text{H}_{31}\text{GeLi}$   
 $\text{Pb}^*\text{C}_{37}\text{H}_{32}\text{Ge}$   
 $\text{Pb}^*\text{Cl}_2$   
 $\text{Pb}^*\text{Cl}_6\text{H}_8\text{N}_2$   
 $\text{Pb}^*\text{Cs}$   
 $\text{Pb}^*\text{K}$   
 $\text{Pb}^*\text{Li}$   
 $\text{Pb}^*\text{Li}_3$   
 $\text{Pb}^*\text{Li}_4$   
 $\text{Pb}^*\text{Na}$   
 $\text{PbPt}^*\text{C}_{60}\text{H}_{50}\text{P}_2$   
**PbRb**  
     RbPb  
         Formation: 5.5.7.1.1  
 $\text{PbRb}^*\text{C}_{18}\text{H}_{15}$   
 $\text{PbS}^*\text{C}_7\text{H}_{16}\text{O}$   
 $\text{PbSi}^*\text{C}_{22}\text{H}_{25}\text{Li}$   
 $\text{PbSi}^*\text{C}_{24}\text{H}_{27}\text{Cl}$   
 $\text{PbSi}^*\text{C}_{37}\text{H}_{30}\text{Cl}_2$   
 $\text{PbSn}^*\text{C}_{37}\text{H}_{30}\text{Cl}_2$   
 $\text{Pb}_2^*\text{Au}$   
 $\text{Pb}_2^*\text{C}_6\text{H}_{18}$   
 $\text{Pb}_2^*\text{C}_{36}\text{H}_{30}$   
 $\text{Pb}_2^*\text{C}_{36}\text{H}_{66}$   
 $\text{Pb}_2^*\text{C}_{37}\text{H}_{30}\text{Cl}_2$   
 $\text{Pb}_2^*\text{C}_{37}\text{H}_{31}\text{Li}$   
 $\text{Pb}_2^*\text{C}_{37}\text{H}_{32}$   
 $\text{Pb}_2^*\text{C}_{42}\text{H}_{42}$   
 $\text{Pb}_2^*\text{C}_{49}\text{H}_{41}\text{As}$   
 $\text{Pb}_2^*\text{C}_{55}\text{H}_{46}\text{Ge}$   
 $\text{Pb}_2^*\text{Hg}$   
 $\text{Pb}_2^*\text{K}$   
 $\text{Pb}_2^*\text{Li}_5$   
 $\text{Pb}_2^*\text{Li}_7$   
 $\text{Pb}_2\text{Pt}^*\text{C}_{72}\text{H}_{60}\text{P}_2$   
 $\text{Pb}_2\text{Si}^*\text{C}_{40}\text{H}_{40}$

$\text{Pb}_3^*\text{C}_{55}\text{H}_{46}$   
 $\text{Pb}_3^*\text{Li}_8$   
 $\text{Pb}_4^*\text{Na}_9$   
 $\text{Pb}_4^*\text{Na}_{15}$   
 $\text{Pb}_5^*\text{Li}_{22}$   
 $\text{Pb}_{83}^*\text{Li}_{17}$   
 $\text{Pd}^*\text{C}_{54}\text{H}_{45}\text{P}_3$   
 $\text{Pd}^*\text{C}_{72}\text{H}_{60}\text{CdGe}_2\text{P}_2$   
 $\text{Pd}^*\text{C}_{72}\text{H}_{60}\text{Ge}_2\text{HgP}_2$   
 $\text{Pr}^*\text{C}_{90}\text{F}_{75}\text{Ge}_5\text{Hg}$   
 $\text{Pt}^*\text{C}_{60}\text{H}_{50}\text{P}_2\text{Pb}$   
 $\text{Pt}^*\text{C}_{72}\text{H}_{60}\text{P}_2\text{Pb}_2$   
 $\text{PtSn}_2^*\text{C}_{78}\text{H}_{36}\text{F}_{30}\text{HgP}_2$   
**Rb**  
     Rb  
         Reaction with  $\text{Ph}_6\text{Pb}_2$ : 5.5.7.2.1  
         Reaction with  $\text{R}_3\text{GeLi}$ : 5.5.5.7  
 $\text{Rb}^*\text{C}_3\text{H}_5$   
 $\text{Rb}^*\text{C}_6\text{H}_6$   
 $\text{Rb}^*\text{C}_8$   
 $\text{Rb}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Rb}^*\text{C}_{13}\text{H}_{11}$   
 $\text{Rb}^*\text{C}_{18}\text{H}_{15}\text{Pb}$   
 $\text{Rb}^*\text{C}_{19}\text{H}_{15}$   
 $\text{Rb}^*\text{C}_{24}$   
 $\text{Rb}^*\text{C}_{36}$   
 $\text{Rb}^*\text{C}_{48}$   
 $\text{Rb}^*\text{C}_{60}$   
 $\text{Rb}^*\text{F}$   
 $\text{Rb}^*\text{Ge}$   
 $\text{Rb}^*\text{GeH}_3$   
 $\text{Rb}^*\text{Pb}$   
**RbSi**  
     RbSi  
         Formation: 5.5.4.1  
 $\text{RbSi}^*\text{C}_4\text{H}_{11}$   
 $\text{RbSi}^*\text{C}_{18}\text{H}_{15}$   
**RbSn**  
     RbSn  
         Formation: 5.5.6.1.4  
 $\text{Re}^*\text{C}_8\text{H}_4\text{BrHgO}_3$   
 $\text{Re}^*\text{C}_8\text{H}_4\text{ClHgO}_3$   
 $\text{Re}^*\text{C}_9\text{H}_4\text{LiO}_3$   
 $\text{Re}^*\text{C}_8\text{H}_6\text{BO}_5$   
 $\text{S}^*\text{CAgF}_3\text{O}_3$   
 $\text{S}^*\text{CCuF}_3\text{O}_3$   
 $\text{S}^*\text{CCuN}$   
 $\text{S}^*\text{C}_2\text{H}_3\text{Li}_2\text{O}$   
 $\text{S}^*\text{C}_2\text{H}_3\text{KO}$   
 $\text{S}^*\text{C}_2\text{H}_3\text{Li}$   
 $\text{S}^*\text{C}_2\text{H}_3\text{LiO}$   
 $\text{S}^*\text{C}_2\text{H}_3\text{LiO}_2$

S*C <sub>2</sub> H <sub>3</sub> LiO <sub>3</sub>	S*C <sub>7</sub> H <sub>3</sub> Li <sub>3</sub> O <sub>2</sub>
S*C <sub>2</sub> H <sub>5</sub> NaO	S*C <sub>7</sub> H <sub>6</sub> ClLiO
S*C <sub>3</sub> HLiN	S*C <sub>7</sub> H <sub>6</sub> Li <sub>2</sub>
S*C <sub>3</sub> H <sub>2</sub> ClHgN	S*C <sub>7</sub> H <sub>6</sub> Li <sub>2</sub> O <sub>2</sub>
S*C <sub>3</sub> H <sub>2</sub> LiN	S*C <sub>7</sub> H <sub>7</sub> ClHgO <sub>2</sub>
S*C <sub>3</sub> H <sub>4</sub> Li <sub>2</sub>	S*C <sub>7</sub> H <sub>7</sub> Li
S*C <sub>3</sub> H <sub>6</sub> LiN	S*C <sub>7</sub> H <sub>7</sub> LiO
S*C <sub>3</sub> H <sub>7</sub> Li <sub>2</sub> NO <sub>2</sub>	S*C <sub>7</sub> H <sub>7</sub> LiO <sub>2</sub>
S*C <sub>3</sub> H <sub>8</sub> LiNO	S*C <sub>7</sub> H <sub>8</sub>
S*C <sub>3</sub> H <sub>8</sub> LiNO <sub>2</sub>	S*C <sub>7</sub> H <sub>9</sub> LiO
S*C <sub>3</sub> H <sub>8</sub> LiO <sub>2</sub> P	S*C <sub>7</sub> H <sub>12</sub> LiNO
S*C <sub>4</sub> Cl <sub>3</sub> Li	S*C <sub>7</sub> H <sub>14</sub> LiN
S*C <sub>4</sub> H <sub>2</sub> BrLi	S*C <sub>7</sub> H <sub>15</sub> GeLiO
S*C <sub>4</sub> H <sub>2</sub> ClLi	S*C <sub>7</sub> H <sub>15</sub> LiO
S*C <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub> Hg <sub>2</sub>	S*C <sub>7</sub> H <sub>16</sub> GeO
S*C <sub>4</sub> H <sub>2</sub> FLi	S*C <sub>7</sub> H <sub>16</sub> OPb
S*C <sub>4</sub> H <sub>2</sub> ILi	S*C <sub>8</sub> H <sub>6</sub> LiN
S*C <sub>4</sub> H <sub>2</sub> Li <sub>2</sub>	S*C <sub>8</sub> H <sub>6</sub> Li <sub>2</sub> O <sub>2</sub>
S*C <sub>4</sub> H <sub>2</sub> Na	S*C <sub>8</sub> H <sub>7</sub> Li
S*C <sub>4</sub> H <sub>3</sub> Cl	S*C <sub>8</sub> H <sub>7</sub> LiO <sub>3</sub>
S*C <sub>4</sub> H <sub>3</sub> ClHg	S*C <sub>8</sub> H <sub>7</sub> Li <sub>2</sub> N
S*C <sub>4</sub> H <sub>3</sub> Li	S*C <sub>8</sub> H <sub>8</sub> LiN
S*C <sub>4</sub> H <sub>5</sub> BO <sub>2</sub>	S*C <sub>8</sub> H <sub>8</sub> LiNO
S*C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	S*C <sub>8</sub> H <sub>9</sub> Li
S*C <sub>4</sub> H <sub>7</sub> Li	S*C <sub>8</sub> H <sub>9</sub> LiO
S*C <sub>4</sub> H <sub>7</sub> LiO	S*C <sub>8</sub> H <sub>9</sub> LiO <sub>3</sub>
S*C <sub>4</sub> H <sub>7</sub> LiO <sub>3</sub>	S*C <sub>8</sub> H <sub>9</sub> Li <sub>2</sub> NO
S*C <sub>4</sub> H <sub>10</sub> O <sub>4</sub>	S*C <sub>8</sub> H <sub>10</sub> HgO <sub>2</sub>
S*C <sub>5</sub> H <sub>6</sub> LiN	S*C <sub>8</sub> H <sub>10</sub> LiNO
S*C <sub>5</sub> H <sub>7</sub> Li	S*C <sub>8</sub> H <sub>10</sub> LiNO <sub>2</sub>
S*C <sub>5</sub> H <sub>7</sub> LiO	S*C <sub>8</sub> H <sub>10</sub> LiP
S*C <sub>5</sub> H <sub>8</sub> LiN	S*C <sub>8</sub> H <sub>13</sub> Li
S*C <sub>5</sub> H <sub>9</sub> LiO	S*C <sub>8</sub> H <sub>14</sub> LiOP
S*C <sub>5</sub> H <sub>9</sub> LiO <sub>3</sub>	S*C <sub>8</sub> H <sub>16</sub> Li <sub>2</sub> O <sub>2</sub>
S*C <sub>5</sub> H <sub>10</sub> LiNO <sub>2</sub>	S*C <sub>9</sub> H <sub>6</sub> Li <sub>2</sub>
S*C <sub>5</sub> H <sub>11</sub> ClLiO <sub>2</sub> P	S*C <sub>9</sub> H <sub>7</sub> Li <sub>2</sub> NO <sub>2</sub>
S*C <sub>5</sub> H <sub>11</sub> ClMg	S*C <sub>9</sub> H <sub>8</sub> Li <sub>2</sub> O <sub>3</sub>
S*C <sub>5</sub> H <sub>11</sub> LiO	S*C <sub>9</sub> H <sub>9</sub> F <sub>3</sub> Li
S*C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> HgO <sub>2</sub>	S*C <sub>9</sub> H <sub>9</sub> Li
S*C <sub>6</sub> H <sub>4</sub> Li <sub>2</sub>	S*C <sub>9</sub> H <sub>9</sub> LiO
S*C <sub>6</sub> H <sub>4</sub> Li <sub>2</sub> O <sub>3</sub>	S*C <sub>9</sub> H <sub>9</sub> LiO <sub>2</sub>
S*C <sub>6</sub> H <sub>5</sub> Li	S*C <sub>9</sub> H <sub>9</sub> Li <sub>2</sub> N
S*C <sub>6</sub> H <sub>6</sub> ClHgNO <sub>2</sub>	S*C <sub>9</sub> H <sub>10</sub> LiNO <sub>3</sub>
S*C <sub>6</sub> H <sub>9</sub> ClFLi	S*C <sub>9</sub> H <sub>11</sub> Li
S*C <sub>6</sub> H <sub>9</sub> Li	S*C <sub>9</sub> H <sub>17</sub> LiO
S*C <sub>6</sub> H <sub>9</sub> LiO <sub>2</sub>	S*C <sub>10</sub> H <sub>11</sub> BrHg <sub>2</sub> O <sub>2</sub>
S*C <sub>6</sub> H <sub>11</sub> ClHgO <sub>2</sub>	S*C <sub>10</sub> H <sub>11</sub> Li
S*C <sub>6</sub> H <sub>11</sub> LiO <sub>2</sub>	S*C <sub>10</sub> H <sub>11</sub> LiO
S*C <sub>6</sub> H <sub>13</sub> ClHgO <sub>2</sub>	S*C <sub>10</sub> H <sub>11</sub> LiO <sub>2</sub>
S*C <sub>6</sub> H <sub>14</sub> LiN	S*C <sub>10</sub> H <sub>12</sub> O
S*C <sub>6</sub> H <sub>14</sub> LiO <sub>3</sub> P	S*C <sub>10</sub> H <sub>13</sub> Li
S*C <sub>6</sub> H <sub>14</sub> LiO <sub>5</sub> P	S*C <sub>10</sub> H <sub>14</sub>

$S^*C_{10}H_{14}O$	$S^*C_{21}H_{17}LiO_2$
$S^*C_{11}H_{11}Li$	$S^*C_{23}H_{20}FeLiP$
$S^*C_{11}H_{13}Li$	$S^*C_{25}H_{20}$
$S^*C_{11}H_{13}LiO_2$	$S^*Na_2$
$S^*C_{11}H_{13}Li_2N_2O_2$	$S^*Na_2O_4$
$S^*C_{11}H_{14}LiN$	$SSi^*C_7H_{15}LiO$
$S^*C_{11}H_{14}O$	$SSi^*C_7H_{16}LiN$
$S^*C_{11}H_{15}Li$	$SSi^*C_7H_{16}O$
$S^*C_{11}H_{16}$	$SSi^*C_{10}H_{15}Li$
$S^*C_{11}H_{16}O$	$SSi^*C_{10}H_{15}LiO$
$S^*C_{11}H_{19}LiO_2$	$SSi^*C_{10}H_{16}$
$S^*C_{12}H_2F_8HgO_3$	$SSi^*C_{11}H_{18}$
$S^*C_{12}H_8$	$SSi^*C_{12}H_{18}$
$S^*C_{12}H_8BrLiO_2$	$SSi^*C_{14}H_{20}$
$S^*C_{12}H_8Cl_2HgO_2$	$SSi^*C_{14}H_{24}$
$S^*C_{12}H_8Li_2$	$SSi^*C_{15}H_{24}O$
$S^*C_{12}H_8Li_2O_2$	$SSi^*C_{15}H_{25}Li$
$S^*C_{12}H_9LiO_2$	$SSi^*C_{16}H_{20}$
$S^*C_{12}H_{10}HgO_2$	$SSi^*C_{16}H_{20}Li$
$S^*C_{12}H_{13}ClHgO_2$	$SSi^*C_{24}H_{35}LiO_5$
$S^*C_{12}H_{14}LiNO_2$	$SSi_2^*C_{12}H_{30}Hg$
$S^*C_{12}H_{14}LiP$	$SSn^*C_7H_{16}O$
$S^*C_{12}H_{16}$	$SSn^*C_{11}H_{16}$
$S^*C_{12}H_{17}Li$	$SSn^*C_{14}H_{32}$
$S^*C_{12}H_{18}$	$SSn^*C_{17}H_{20}$
$S^*C_{12}H_{19}AuCl_2$	$SSn^*C_{17}H_{36}O$
$S^*C_{13}H_{11}Li$	$SSn^*C_{23}H_{24}$
$S^*C_{13}H_{12}HgO_2$	$SSn^*C_{26}H_{24}$
$S^*C_{13}H_{15}Li$	$SW^*C_{21}H_{15}LiO_4$
$S^*C_{13}H_{18}LiP$	$SZn^*C_4H_{10}O_4$
$S^*C_{13}H_{20}$	$S_2^*C_2CdN_2$
$S^*C_{14}H_{11}Li$	$S_2^*C_3H_7Li$
$S^*C_{14}H_{13}Li$	$S_2^*C_3H_7LiO$
$S^*C_{14}H_{14}$	$S_2^*C_4H_3Li$
$S^*C_{14}H_{17}Li$	$S_2^*C_4H_6LiN$
$S^*C_{14}H_{19}LiO$	$S_2^*C_4H_7Li$
$S^*C_{14}H_{22}$	$S_2^*C_4H_7LiO$
$S^*C_{15}H_{13}LiO_3$	$S_2^*C_4H_8LiN$
$S^*C_{15}H_{16}$	$S_2^*C_4H_9LiO$
$S^*C_{16}H_{18}$	$S_2^*C_5H_5Li$
$S^*C_{16}H_{18}LiNO_2$	$S_2^*C_5H_6LiN$
$S^*C_{16}H_{18}O$	$S_2^*C_5H_9Li$
$S^*C_{17}H_{14}Li_2O_2$	$S_2^*C_6H_8Li_2$
$S^*C_{18}H_{27}LiO$	$S_2^*C_6H_9Li$
$S^*C_{19}H_{16}$	$S_2^*C_6H_{10}LiN$
$S^*C_{19}H_{16}LiOP$	$S_2^*C_6H_{11}Li$
$S^*C_{20}H_{15}Li$	$S_2^*C_6H_{11}LiO$
$S^*C_{20}H_{18}$	$S_2^*C_7H_5Li$
$S^*C_{21}H_{15}CrLiO_4$	$S_2^*C_7H_{12}LiNO$
$S^*C_{21}H_{15}LiMoO_4$	$S_2^*C_8H_{15}LiO$
$S^*C_{21}H_{17}Li$	$S_2^*C_9H_{10}LiN$
$S^*C_{21}H_{17}LiO$	$S_2^*C_9H_{12}LiNO_3$

$S_2^*C_9H_{13}Li$	$S_4^*C_4H_7Li$
$S_2^*C_9H_{15}Li$	$S_4^*C_6H_3Li$
$S_2^*C_9H_{15}LiO$	$S_4^*C_6H_{12}$
$S_2^*C_9H_{17}Li$	$S_4^*C_{11}H_{21}LiN_2$
$S_2^*C_{12}H_4Cl_{10}HgO_8$	$S_4^*C_{25}H_{20}$
$S_2^*C_{12}H_4F_{10}HgO_8$	$S_4^*C_{26}H_{22}Hg$
$S_2^*C_{12}H_6Cl_8HgO_8$	$Sb^*C_6H_4Cl_3$
$S_2^*C_{12}H_6F_8HgO_8$	$Sb^*C_{12}H_{10}Li$
$S_2^*C_{12}H_8F_2HgO_4$	$Sb^*C_{13}H_{12}Li$
$S_2^*C_{12}H_{10}HgO_4$	$Sb^*C_{18}H_{12}Br_3$
$S_2^*C_{12}H_{13}LiO$	$Sb^*C_{18}H_{12}Cl_3$
$S_2^*C_{13}H_{11}Li$	$Sb^*C_{18}H_{15}$
$S_2^*C_{13}H_{12}$	$Sb^*C_{21}H_{21}$
$S_2^*C_{13}H_{15}LiO$	$Sb^*C_{24}H_{20}Br$
$S_2^*C_{14}H_{13}Li$	$Sb^*C_{36}H_{27}$
$S_2^*C_{14}H_{14}$	$Sb_2^*C_{23}H_{21}Li$
$S_2^*C_{14}H_{14}Hg$	$Sb_2^*C_{25}H_{22}$
$S_2^*C_{14}H_{14}HgO_4$	$Sb_3^*C_{37}H_{31}$
$S_2^*C_{14}H_{14}LiNO_3$	$Se^*C_4H_3Li$
$S_2^*C_{15}H_{14}$	$Se^*C_5H_2LiN$
$S_2^*C_{15}H_{14}HgO_6$	$Se^*C_5H_{12}$
$S_2^*C_{15}H_{16}$	$Se^*C_6H_3Li$
$S_2^*C_{16}H_{10}Hg$	$Se^*C_7H_7Li$
$S_2^*C_{16}H_{16}$	$Se^*C_7H_7LiO$
$S_2^*C_{16}H_{18}$	$Se^*C_7H_8$
$S_2^*C_{16}H_{23}Li$	$Se^*C_8H_6F_3Li$
$S_2^*C_{17}H_{16}Hg_2O_8$	$Se^*C_8H_6Li_2O_2$
$S_2^*C_{17}H_{18}$	$Se^*C_8H_7Li$
$S_2^*C_{17}H_{20}$	$Se^*C_8H_9LiO$
$S_2^*C_{18}H_2Cl_{12}Hg_2O_6$	$Se^*C_9H_6F_3Li$
$S_2^*C_{18}H_2F_{12}Hg_2O_6$	$Se^*C_9H_6Li_2$
$S_2^*C_{18}H_{22}$	$Se^*C_9H_8F_3LiO$
$S_2^*C_{18}H_{22}O$	$Se^*C_9H_9Li$
$S_2^*C_{19}H_{16}$	$Se^*C_9H_9LiO_2$
$S_2^*C_{19}H_{20}$	$Se^*C_9H_{11}LiO$
$S_2^*C_{20}H_{22}$	$Se^*C_9H_{13}LiO_2$
$S_2^*C_{22}H_{10}F_{10}HgN_2O_6$	$Se^*C_{10}H_8F_3Li$
$S_2^*C_{22}H_{10}HgN_2O_6$	$Se^*C_{10}H_{11}Li$
$S_2^*C_{22}H_{12}Cl_8HgN_2O_6$	$Se^*C_{11}H_{11}LiO$
$S_2^*C_{22}H_{12}F_8HgN_2O_6$	$Se^*C_{11}H_{11}LiO_2$
$S_2^*C_{22}H_{22}$	$Se^*C_{11}H_{15}Li$
$S_2^*C_{30}H_{30}$	$Se^*C_{12}H_{17}Li$
$S_2^*C_{34}H_{40}Ag_4Au_2F_6N_4O_6$	$Se^*C_{13}H_{11}Li$
$S_2Si^*C_7H_{15}Li$	$Se^*C_{13}H_{11}LiO$
$S_2Sn^*C_6H_{15}Li$	$Se^*C_{14}H_{11}Li$
$S_2Zn^*C_{10}H_{22}$	$Se^*C_{14}H_{11}LiO$
$S_2Zn^*C_{14}H_{14}$	$Se^*C_{14}H_{13}Li$
$S_3^*C_3H_5Li$	$Se^*C_{14}H_{13}LiO$
$S_3^*C_3H_9Li$	$Se^*C_{14}H_{17}LiO$
$S_3^*C_5H_{10}LiN$	$Se^*C_{14}H_{18}LiN$
$S_3^*C_{19}H_{15}Li$	$Se^*C_{15}H_{15}LiO$
$S_3^*C_{55}H_{45}Li$	$Se^*C_{17}H_{27}LiO$

SeSi*C <sub>6</sub> H <sub>16</sub>	Si*C <sub>5</sub> H <sub>13</sub> LiO
SeSi*C <sub>7</sub> H <sub>16</sub>	Si*C <sub>6</sub> H <sub>11</sub> Cl <sub>2</sub> Li
SeSi*C <sub>10</sub> H <sub>15</sub> Li	Si*C <sub>6</sub> H <sub>11</sub> Li
SeSi*C <sub>11</sub> H <sub>14</sub> F <sub>3</sub> Li	Si*C <sub>6</sub> H <sub>12</sub> ClLi
Se <sub>2</sub> *C <sub>13</sub> H <sub>11</sub> Li	Si*C <sub>6</sub> H <sub>12</sub> Hg
Se <sub>2</sub> *C <sub>13</sub> H <sub>12</sub>	Si*C <sub>6</sub> H <sub>13</sub> Li
Se <sub>2</sub> *C <sub>14</sub> H <sub>13</sub> Li	Si*C <sub>6</sub> H <sub>13</sub> LiO
Se <sub>2</sub> *C <sub>14</sub> H <sub>14</sub> O	Si*C <sub>6</sub> H <sub>15</sub> Cs
Se <sub>2</sub> *C <sub>15</sub> H <sub>14</sub>	Si*C <sub>6</sub> H <sub>15</sub> K
Se <sub>2</sub> *C <sub>16</sub> H <sub>16</sub>	Si*C <sub>6</sub> H <sub>15</sub> Li
Se <sub>2</sub> *C <sub>19</sub> H <sub>23</sub> Li	Si*C <sub>6</sub> H <sub>15</sub> Na
Se <sub>2</sub> *C <sub>20</sub> H <sub>16</sub>	Si*C <sub>6</sub> H <sub>16</sub>
Se <sub>3</sub> *C <sub>19</sub> H <sub>15</sub> Li	Si*C <sub>6</sub> H <sub>16</sub> Se
Se <sub>3</sub> *C <sub>19</sub> H <sub>16</sub>	Si*C <sub>6</sub> H <sub>18</sub> GeHg
Se <sub>3</sub> *C <sub>20</sub> H <sub>18</sub>	Si*C <sub>7</sub> H <sub>7</sub> Cl <sub>4</sub> N
Se <sub>4</sub> *C <sub>25</sub> H <sub>20</sub>	Si*C <sub>7</sub> H <sub>12</sub> HgO <sub>2</sub>
Si*BrCl <sub>3</sub> Hg	Si*C <sub>7</sub> H <sub>14</sub> LiNO
Si*BrH <sub>3</sub>	Si*C <sub>7</sub> H <sub>15</sub> LiO
Si*CH <sub>4</sub> Cl <sub>2</sub>	Si*C <sub>7</sub> H <sub>15</sub> LiOS
Si*C <sub>2</sub> H <sub>5</sub> Cl <sub>3</sub> Hg	Si*C <sub>7</sub> H <sub>15</sub> LiO <sub>2</sub>
Si*C <sub>2</sub> H <sub>6</sub> Hg	Si*C <sub>7</sub> H <sub>15</sub> LiS <sub>2</sub>
Si*C <sub>2</sub> H <sub>7</sub> Cl	Si*C <sub>7</sub> H <sub>15</sub> N
Si*C <sub>3</sub> H <sub>9</sub> Br	Si*C <sub>7</sub> H <sub>16</sub> LiNO
Si*C <sub>3</sub> H <sub>9</sub> Cl	Si*C <sub>7</sub> H <sub>16</sub> LiNS
Si*C <sub>3</sub> H <sub>9</sub> Cl <sub>3</sub> GeHg	Si*C <sub>7</sub> H <sub>16</sub> OS
Si*C <sub>3</sub> H <sub>9</sub> K	Si*C <sub>7</sub> H <sub>16</sub> Se
Si*C <sub>3</sub> H <sub>9</sub> Li	Si*C <sub>7</sub> H <sub>17</sub> LiO
Si*C <sub>3</sub> H <sub>9</sub> Na	Si*C <sub>8</sub> H <sub>7</sub> Cl <sub>5</sub>
Si*C <sub>3</sub> H <sub>9</sub> NaO	Si*C <sub>8</sub> H <sub>7</sub> F <sub>5</sub>
Si*C <sub>3</sub> H <sub>9</sub> NaO <sub>2</sub>	Si*C <sub>8</sub> H <sub>11</sub> Cl
Si*C <sub>4</sub> H <sub>9</sub> Br <sub>2</sub> Li	Si*C <sub>8</sub> H <sub>11</sub> Li
Si*C <sub>4</sub> H <sub>9</sub> Cl <sub>2</sub> Li	Si*C <sub>8</sub> H <sub>14</sub> LiNO
Si*C <sub>4</sub> H <sub>9</sub> LiN <sub>2</sub>	Si*C <sub>8</sub> H <sub>15</sub> Li
Si*C <sub>4</sub> H <sub>10</sub> ClLi	Si*C <sub>8</sub> H <sub>17</sub> ClHg
Si*C <sub>4</sub> H <sub>11</sub> Cl	Si*C <sub>8</sub> H <sub>18</sub> ClLi
Si*C <sub>4</sub> H <sub>11</sub> ClHg	Si*C <sub>8</sub> H <sub>19</sub> Li
Si*C <sub>4</sub> H <sub>11</sub> ClMg	Si*C <sub>8</sub> H <sub>20</sub> Hg
Si*C <sub>4</sub> H <sub>11</sub> Cl <sub>3</sub> GeHg	Si*C <sub>9</sub> H <sub>11</sub> ClFLi
Si*C <sub>4</sub> H <sub>11</sub> Cs	Si*C <sub>9</sub> H <sub>14</sub>
Si*C <sub>4</sub> H <sub>11</sub> K	Si*C <sub>9</sub> H <sub>18</sub> ClLiO <sub>2</sub>
Si*C <sub>4</sub> H <sub>11</sub> Li	Si*C <sub>9</sub> H <sub>19</sub> Li
Si*C <sub>4</sub> H <sub>11</sub> LiO	Si*C <sub>9</sub> H <sub>19</sub> LiO
Si*C <sub>4</sub> H <sub>11</sub> Na	Si*C <sub>9</sub> H <sub>19</sub> LiO <sub>2</sub>
Si*C <sub>4</sub> H <sub>11</sub> Rb	Si*C <sub>9</sub> H <sub>21</sub> Li
Si*C <sub>4</sub> H <sub>12</sub>	Si*C <sub>10</sub> H <sub>13</sub> Li
Si*C <sub>4</sub> H <sub>12</sub> O	Si*C <sub>10</sub> H <sub>15</sub> LiOS
Si*C <sub>5</sub> H <sub>10</sub> LiN	Si*C <sub>10</sub> H <sub>15</sub> LiS
Si*C <sub>5</sub> H <sub>10</sub> Li <sub>2</sub> O <sub>2</sub>	Si*C <sub>10</sub> H <sub>15</sub> LiSe
Si*C <sub>5</sub> H <sub>11</sub> Li	Si*C <sub>10</sub> H <sub>16</sub> S
Si*C <sub>5</sub> H <sub>11</sub> LiO	Si*C <sub>10</sub> H <sub>22</sub> BLiO <sub>2</sub>
Si*C <sub>5</sub> H <sub>12</sub>	Si*C <sub>11</sub> H <sub>14</sub> F <sub>3</sub> LiSe
Si*C <sub>5</sub> H <sub>13</sub> Li	Si*C <sub>11</sub> H <sub>14</sub> LiNO

Si*C <sub>11</sub> H <sub>18</sub> S	Si*C <sub>21</sub> H <sub>21</sub> K
Si*C <sub>11</sub> H <sub>23</sub> LiO	Si*C <sub>21</sub> H <sub>22</sub>
Si*C <sub>11</sub> H <sub>27</sub> N	Si*C <sub>21</sub> H <sub>27</sub> Li
Si*C <sub>12</sub> H <sub>5</sub> F <sub>9</sub>	Si*C <sub>22</sub> H <sub>25</sub> LiPb
Si*C <sub>12</sub> H <sub>11</sub> Cl	Si*C <sub>24</sub> H <sub>20</sub>
Si*C <sub>12</sub> H <sub>11</sub> Li	Si*C <sub>24</sub> H <sub>27</sub> ClPb
Si*C <sub>12</sub> H <sub>12</sub>	Si*C <sub>24</sub> H <sub>30</sub> Ge
Si*C <sub>12</sub> H <sub>18</sub> S	Si*C <sub>24</sub> H <sub>35</sub> LiO <sub>5</sub> S
Si*C <sub>12</sub> H <sub>19</sub> Cl	Si*C <sub>25</sub> H <sub>22</sub>
Si*C <sub>12</sub> H <sub>19</sub> Li	Si*C <sub>26</sub> H <sub>22</sub>
Si*C <sub>12</sub> H <sub>20</sub>	Si*C <sub>26</sub> H <sub>23</sub> Li
Si*C <sub>12</sub> H <sub>21</sub> LiO	Si*C <sub>27</sub> H <sub>26</sub>
Si*C <sub>12</sub> H <sub>24</sub> O <sub>3</sub>	Si*C <sub>30</sub> H <sub>26</sub>
Si*C <sub>12</sub> H <sub>25</sub> LiO	Si*C <sub>30</sub> H <sub>26</sub> Li <sub>2</sub>
Si*C <sub>12</sub> H <sub>27</sub> Br	Si*C <sub>30</sub> H <sub>26</sub> Li <sub>4</sub>
Si*C <sub>12</sub> H <sub>27</sub> Li	Si*C <sub>36</sub> H <sub>30</sub> AuP
Si*C <sub>12</sub> H <sub>27</sub> Na	Si*C <sub>37</sub> H <sub>30</sub>
Si*C <sub>12</sub> H <sub>28</sub>	Si*C <sub>37</sub> H <sub>30</sub> Cl <sub>2</sub> Pb
Si*C <sub>12</sub> H <sub>30</sub> GeHg	Si*C <sub>40</sub> H <sub>40</sub> Pb <sub>2</sub>
Si*C <sub>13</sub> H <sub>13</sub> Cl	Si*C <sub>54</sub> H <sub>45</sub> Ge <sub>3</sub> Li
Si*C <sub>13</sub> H <sub>13</sub> Li	Si*C <sub>54</sub> H <sub>46</sub> Ge <sub>3</sub>
Si*C <sub>13</sub> H <sub>13</sub> Na	Si*ClH <sub>3</sub>
Si*C <sub>14</sub> H <sub>20</sub> S	Si*Cl <sub>3</sub> H
Si*C <sub>14</sub> H <sub>24</sub> S	Si*Cl <sub>3</sub> HgI
Si*C <sub>15</sub> H <sub>16</sub>	Si*Cl <sub>4</sub>
Si*C <sub>15</sub> H <sub>24</sub> OS	Si*C <sub>s</sub>
Si*C <sub>15</sub> H <sub>25</sub> LiS	Si*C <sub>u</sub> <sub>5</sub>
Si*C <sub>16</sub> H <sub>19</sub> Cl	Si*C <sub>u</sub> <sub>6</sub>
Si*C <sub>16</sub> H <sub>19</sub> Li	Si*H <sub>3</sub> K
Si*C <sub>16</sub> H <sub>20</sub> LiS	Si*H <sub>4</sub>
Si*C <sub>16</sub> H <sub>20</sub> S	Si*K
Si*C <sub>17</sub> H <sub>16</sub>	Si*Li <sub>2</sub>
Si*C <sub>17</sub> H <sub>17</sub> Li	Si*Li <sub>4</sub>
Si*C <sub>18</sub> H <sub>10</sub> ClF <sub>5</sub>	Si*Na
Si*C <sub>18</sub> H <sub>15</sub> Cl	Si*Rb
Si*C <sub>18</sub> H <sub>15</sub> Cs	SiSn*C <sub>6</sub> H <sub>18</sub> Hg
Si*C <sub>18</sub> H <sub>15</sub> F	SiSn*C <sub>7</sub> H <sub>20</sub> O
Si*C <sub>18</sub> H <sub>15</sub> K	SiSn*C <sub>16</sub> H <sub>38</sub>
Si*C <sub>18</sub> H <sub>15</sub> Li	SiSn*C <sub>17</sub> H <sub>38</sub>
Si*C <sub>18</sub> H <sub>15</sub> Na	SiSn*C <sub>23</sub> H <sub>26</sub>
Si*C <sub>18</sub> H <sub>15</sub> Rb	SiSn*C <sub>23</sub> H <sub>50</sub> O
Si*C <sub>18</sub> H <sub>16</sub>	SiSn*C <sub>24</sub> H <sub>48</sub> O
Si*C <sub>18</sub> H <sub>17</sub> N	SiSn*C <sub>24</sub> H <sub>52</sub> O
Si*C <sub>18</sub> H <sub>18</sub>	SiZn <sub>2</sub> *C <sub>4</sub> H <sub>10</sub> Br <sub>2</sub>
Si*C <sub>18</sub> H <sub>18</sub> Li <sub>2</sub>	Si <sub>2</sub> *CCl <sub>7</sub> Li
Si*C <sub>18</sub> H <sub>25</sub> CrLiO <sub>4</sub>	Si <sub>2</sub> *C <sub>2</sub> H <sub>6</sub> Cl <sub>4</sub> Hg
Si*C <sub>20</sub> H <sub>17</sub> LiO	Si <sub>2</sub> *C <sub>3</sub> H <sub>9</sub> Cl <sub>3</sub>
Si*C <sub>20</sub> H <sub>18</sub>	Si <sub>2</sub> *C <sub>3</sub> H <sub>9</sub> Cl <sub>3</sub> Hg
Si*C <sub>20</sub> H <sub>19</sub> Cl	Si <sub>2</sub> *C <sub>3</sub> H <sub>12</sub> Hg
Si*C <sub>20</sub> H <sub>19</sub> Li	Si <sub>2</sub> *C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub>
Si*C <sub>21</sub> H <sub>20</sub>	Si <sub>2</sub> *C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub> Hg
Si*C <sub>21</sub> H <sub>21</sub> Cl	Si <sub>2</sub> *C <sub>4</sub> H <sub>14</sub> Hg



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$\text{Si}_2^*\text{C}_5\text{H}_{14}\text{Cl}_2$	$\text{Si}_2^*\text{C}_{42}\text{H}_{42}$
$\text{Si}_2^*\text{C}_6\text{H}_{16}\text{Hg}$	$\text{Si}_2^*\text{Cl}_6$
$\text{Si}_2^*\text{C}_6\text{H}_{18}$	$\text{Si}_2^*\text{Cl}_6\text{Hg}$
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{Hg}$	$\text{Si}_2^*\text{H}_6\text{Hg}$
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{NNa}$	$\text{Si}_2^*\text{Li}_{17}$
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{O}_2$	$\text{Si}_2\text{Zn}^*\text{C}_8\text{H}_{22}$
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{O}_4$	$\text{Si}_2\text{Zn}^*\text{C}_{12}\text{H}_{30}$
$\text{Si}_2^*\text{C}_6\text{H}_{19}\text{N}$	$\text{Si}_3^*\text{C}_{10}\text{H}_{27}\text{Li}$
$\text{Si}_2^*\text{C}_7\text{H}_{18}$	$\text{Si}_3^*\text{C}_{12}\text{H}_{23}\text{Li}$
$\text{Si}_2^*\text{C}_7\text{H}_{18}\text{BrLi}$	$\text{Si}_3^*\text{C}_{12}\text{H}_{33}\text{GeLi}$
$\text{Si}_2^*\text{C}_7\text{H}_{19}\text{BrHg}$	$\text{Si}_3^*\text{C}_{16}\text{H}_{40}\text{Hg}$
$\text{Si}_2^*\text{C}_7\text{H}_{19}\text{Li}$	$\text{Si}_3^*\text{C}_{18}\text{H}_{28}$
$\text{Si}_2^*\text{C}_7\text{H}_{20}$	$\text{Si}_3^*\text{C}_{21}\text{H}_{57}\text{HgLiO}_6$
$\text{Si}_2^*\text{C}_7\text{H}_{21}\text{HgN}$	$\text{Si}_3^*\text{C}_{38}\text{H}_{36}$
$\text{Si}_2^*\text{C}_8\text{H}_{22}\text{Cd}$	$\text{Si}_3^*\text{C}_{48}\text{H}_{40}$
$\text{Si}_2^*\text{C}_8\text{H}_{22}\text{Ge}_2\text{Hg}$	$\text{Si}_3^*\text{Li}_{10}$
$\text{Si}_2^*\text{C}_8\text{H}_{22}\text{Hg}$	$\text{Si}_3\text{Sn}^*\text{C}_{12}\text{H}_{33}\text{Li}$
$\text{Si}_2^*\text{C}_9\text{H}_{19}\text{LiO}_4$	$\text{Si}_3\text{Sn}^*\text{C}_{12}\text{H}_{34}$
$\text{Si}_2^*\text{C}_{10}\text{H}_{22}\text{Hg}$	$\text{Si}_3\text{Sn}_2^*\text{C}_{30}\text{H}_{33}\text{F}_{15}$
$\text{Si}_2^*\text{C}_{10}\text{H}_{25}\text{K}$	$\text{Si}_3\text{Tl}^*\text{C}_{12}\text{H}_{33}\text{Ge}_3$
$\text{Si}_2^*\text{C}_{10}\text{H}_{26}$	$\text{Si}_3\text{Tl}^*\text{C}_{36}\text{H}_{99}$
$\text{Si}_2^*\text{C}_{11}\text{H}_{23}\text{HgN}$	$\text{Si}_4^*\text{C}_6\text{H}_{21}\text{Li}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{27}\text{LiO}_2$	$\text{Si}_4^*\text{C}_9\text{H}_{27}\text{Li}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{29}\text{Li}$	$\text{Si}_4^*\text{C}_{10}\text{H}_{28}\text{Hg}_2$
$\text{Si}_2^*\text{C}_{12}\text{H}_{30}\text{Cd}$	$\text{Si}_4^*\text{C}_{10}\text{H}_{30}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{30}\text{Hg}$	$\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{CdN}_2$
$\text{Si}_2^*\text{C}_{12}\text{H}_{30}\text{HgS}$	$\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{HgN}_2$
$\text{Si}_2^*\text{C}_{14}\text{H}_{38}\text{Hg}$	$\text{Si}_4^*\text{C}_{13}\text{H}_{35}\text{Li}$
$\text{Si}_2^*\text{C}_{16}\text{H}_{12}\text{F}_{10}\text{Hg}$	$\text{Si}_4^*\text{C}_{14}\text{H}_{38}\text{Cd}$
$\text{Si}_2^*\text{C}_{16}\text{H}_{20}$	$\text{Si}_4^*\text{C}_{14}\text{H}_{38}\text{Hg}$
$\text{Si}_2^*\text{C}_{16}\text{H}_{22}$	$\text{Si}_4^*\text{C}_{16}\text{H}_{44}\text{Cu}_4$
$\text{Si}_2^*\text{C}_{16}\text{H}_{22}\text{Hg}$	$\text{Si}_4^*\text{C}_{21}\text{H}_{51}\text{LiO}_3$
$\text{Si}_2^*\text{C}_{17}\text{H}_{38}\text{AgClP}_2$	$\text{Si}_4^*\text{C}_{28}\text{H}_{76}\text{HgLi}_2\text{O}_8$
$\text{Si}_2^*\text{C}_{18}\text{H}_{33}\text{Li}$	$\text{Si}_4^*\text{C}_{48}\text{H}_{40}$
$\text{Si}_2^*\text{C}_{19}\text{H}_{28}\text{LiP}$	$\text{Si}_4^*\text{C}_{48}\text{H}_{40}\text{Li}_2$
$\text{Si}_2^*\text{C}_{20}\text{H}_{30}$	$\text{Si}_4^*\text{C}_{48}\text{H}_{40}\text{Na}_2$
$\text{Si}_2^*\text{C}_{20}\text{H}_{30}\text{Hg}$	$\text{Si}_4^*\text{C}_{49}\text{H}_{43}\text{Li}$
$\text{Si}_2^*\text{C}_{21}\text{H}_{24}$	$\text{Si}_4^*\text{Cu}_{15}$
$\text{Si}_2^*\text{C}_{22}\text{H}_{34}$	$\text{Si}_4\text{Sn}^*\text{C}_{16}\text{H}_{44}$
$\text{Si}_2^*\text{C}_{24}\text{H}_{22}$	$\text{Si}_4\text{Zn}^*\text{C}_{12}\text{H}_{36}\text{N}_2$
$\text{Si}_2^*\text{C}_{24}\text{H}_{30}\text{Hg}$	$\text{Si}_5^*\text{C}_8\text{H}_{28}$
$\text{Si}_2^*\text{C}_{24}\text{H}_{38}$	$\text{Si}_5^*\text{C}_{12}\text{H}_{36}$
$\text{Si}_2^*\text{C}_{24}\text{H}_{54}\text{Cd}$	$\text{Si}_5^*\text{C}_{60}\text{H}_{50}$
$\text{Si}_2^*\text{C}_{24}\text{H}_{54}\text{Hg}$	$\text{Si}_5^*\text{C}_{60}\text{H}_{50}\text{Li}_2$
$\text{Si}_2^*\text{C}_{24}\text{H}_{66}\text{Hg}$	$\text{Si}_6^*\text{C}_{12}\text{H}_{36}$
$\text{Si}_2^*\text{C}_{25}\text{H}_{23}\text{Li}$	$\text{Si}_6^*\text{C}_{20}\text{H}_{54}\text{Cd}$
$\text{Si}_2^*\text{C}_{26}\text{H}_{26}$	$\text{Si}_6^*\text{C}_{24}\text{H}_{66}\text{Ge}_2\text{Hg}$
$\text{Si}_2^*\text{C}_{30}\text{H}_{25}\text{Li}$	$\text{Si}_6^*\text{C}_{72}\text{H}_{60}$
$\text{Si}_2^*\text{C}_{34}\text{H}_{30}\text{Hg}$	$\text{Si}_6^*\text{C}_{72}\text{H}_{60}\text{Li}_2$
$\text{Si}_2^*\text{C}_{36}\text{H}_{30}$	$\text{Si}_6\text{Sn}_2^*\text{C}_{24}\text{H}_{66}\text{Cd}$
$\text{Si}_2^*\text{C}_{36}\text{H}_{30}\text{Hg}$	$\text{Si}_6\text{Sn}_2^*\text{C}_{24}\text{H}_{66}\text{Hg}$
$\text{Si}_2^*\text{C}_{40}\text{H}_{36}\text{Li}_2$	$\text{Si}_6\text{Sn}_2^*\text{C}_{24}\text{H}_{66}\text{O}$

$\text{Si}_6\text{Zn}^*\text{C}_{20}\text{H}_{54}$	$\text{Sn}^*\text{C}_9\text{H}_{22}$
$\text{Si}_8^*\text{C}_{18}\text{H}_{54}$	$\text{Sn}^*\text{C}_9\text{H}_{22}\text{Hg}$
$\text{Sn}^*\text{Ag}_3$	$\text{Sn}^*\text{C}_{10}\text{H}_9\text{F}_9$
$\text{Sn}^*\text{Au}_4$	$\text{Sn}^*\text{C}_{10}\text{H}_{18}$
$\text{Sn}^*\text{CH}_5\text{Na}$	$\text{Sn}^*\text{C}_{10}\text{H}_{24}\text{Hg}$
$\text{Sn}^*\text{C}_2\text{H}_6$	$\text{Sn}^*\text{C}_{11}\text{H}_{16}\text{S}$
$\text{Sn}^*\text{C}_2\text{H}_6\text{Na}_2$	$\text{Sn}^*\text{C}_{11}\text{H}_{17}\text{Li}$
$\text{Sn}^*\text{C}_2\text{H}_7\text{Na}$	$\text{Sn}^*\text{C}_{11}\text{H}_{22}$
$\text{Sn}^*\text{C}_3\text{H}_9\text{Br}$	$\text{Sn}^*\text{C}_{12}\text{H}_{10}$
$\text{Sn}^*\text{C}_3\text{H}_9\text{Cl}$	$\text{Sn}^*\text{C}_{12}\text{H}_{10}\text{Cl}_2$
$\text{Sn}^*\text{C}_3\text{H}_9\text{K}$	$\text{Sn}^*\text{C}_{12}\text{H}_{10}\text{Li}_2$
$\text{Sn}^*\text{C}_3\text{H}_9\text{Li}$	$\text{Sn}^*\text{C}_{12}\text{H}_{10}\text{Na}_2$
$\text{Sn}^*\text{C}_3\text{H}_9\text{Na}$	$\text{Sn}^*\text{C}_{12}\text{H}_{11}\text{Na}$
$\text{Sn}^*\text{C}_3\text{H}_{10}$	$\text{Sn}^*\text{C}_{12}\text{H}_{12}$
$\text{Sn}^*\text{C}_4\text{H}_9\text{BrClLi}$	$\text{Sn}^*\text{C}_{12}\text{H}_{18}$
$\text{Sn}^*\text{C}_4\text{H}_9\text{Br}_2\text{Li}$	$\text{Sn}^*\text{C}_{12}\text{H}_{20}$
$\text{Sn}^*\text{C}_4\text{H}_9\text{Cl}_2\text{Li}$	$\text{Sn}^*\text{C}_{12}\text{H}_{22}\text{Na}_2$
$\text{Sn}^*\text{C}_4\text{H}_{10}\text{Cl}_2$	$\text{Sn}^*\text{C}_{12}\text{H}_{24}$
$\text{Sn}^*\text{C}_4\text{H}_{10}\text{Na}_2$	$\text{Sn}^*\text{C}_{12}\text{H}_{26}$
$\text{Sn}^*\text{C}_4\text{H}_{12}$	$\text{Sn}^*\text{C}_{12}\text{H}_{27}\text{Li}$
$\text{Sn}^*\text{C}_4\text{H}_{12}\text{O}$	$\text{Sn}^*\text{C}_{12}\text{H}_{27}\text{Na}$
$\text{Sn}^*\text{C}_5\text{H}_{11}\text{Cl}$	$\text{Sn}^*\text{C}_{12}\text{H}_{28}$
$\text{Sn}^*\text{C}_6\text{H}_7\text{Na}$	$\text{Sn}^*\text{C}_{12}\text{H}_{28}\text{O}_4$
$\text{Sn}^*\text{C}_6\text{H}_9\text{Na}$	$\text{Sn}^*\text{C}_{12}\text{H}_{33}\text{LiSi}_3$
$\text{Sn}^*\text{C}_6\text{H}_{12}$	$\text{Sn}^*\text{C}_{12}\text{H}_{34}\text{Si}_3$
$\text{Sn}^*\text{C}_6\text{H}_{12}\text{F}_2$	$\text{Sn}^*\text{C}_{13}\text{H}_{13}\text{Li}$
$\text{Sn}^*\text{C}_6\text{H}_{14}$	$\text{Sn}^*\text{C}_{13}\text{H}_{14}$
$\text{Sn}^*\text{C}_6\text{H}_{14}\text{Cl}_2\text{Hg}$	$\text{Sn}^*\text{C}_{13}\text{H}_{23}\text{Li}$
$\text{Sn}^*\text{C}_6\text{H}_{14}\text{Na}_2$	$\text{Sn}^*\text{C}_{13}\text{H}_{24}$
$\text{Sn}^*\text{C}_6\text{H}_{15}\text{Br}$	$\text{Sn}^*\text{C}_{14}\text{H}_{15}\text{Na}$
$\text{Sn}^*\text{C}_6\text{H}_{15}\text{Cl}$	$\text{Sn}^*\text{C}_{14}\text{H}_{27}\text{Li}$
$\text{Sn}^*\text{C}_6\text{H}_{15}\text{Li}$	$\text{Sn}^*\text{C}_{14}\text{H}_{29}\text{Li}$
$\text{Sn}^*\text{C}_6\text{H}_{15}\text{LiS}_2$	$\text{Sn}^*\text{C}_{14}\text{H}_{32}\text{O}$
$\text{Sn}^*\text{C}_6\text{H}_{15}\text{Na}$	$\text{Sn}^*\text{C}_{14}\text{H}_{32}\text{S}$
$\text{Sn}^*\text{C}_6\text{H}_{16}$	$\text{Sn}^*\text{C}_{15}\text{H}_{34}$
$\text{Sn}^*\text{C}_6\text{H}_{18}\text{HgSi}$	$\text{Sn}^*\text{C}_{15}\text{H}_{34}\text{O}$
$\text{Sn}^*\text{C}_7\text{H}_{12}$	$\text{Sn}^*\text{C}_{15}\text{H}_{35}\text{N}$
$\text{Sn}^*\text{C}_7\text{H}_{16}$	$\text{Sn}^*\text{C}_{16}\text{H}_{19}\text{Li}$
$\text{Sn}^*\text{C}_7\text{H}_{16}\text{OS}$	$\text{Sn}^*\text{C}_{16}\text{H}_{28}$
$\text{Sn}^*\text{C}_7\text{H}_{18}\text{Hg}$	$\text{Sn}^*\text{C}_{16}\text{H}_{36}\text{Hg}$
$\text{Sn}^*\text{C}_7\text{H}_{20}\text{OSi}$	$\text{Sn}^*\text{C}_{16}\text{H}_{36}\text{O}_4$
$\text{Sn}^*\text{C}_8\text{F}_{12}$	$\text{Sn}^*\text{C}_{16}\text{H}_{37}\text{NO}$
$\text{Sn}^*\text{C}_8\text{H}_{12}$	$\text{Sn}^*\text{C}_{16}\text{H}_{38}\text{Si}$
$\text{Sn}^*\text{C}_8\text{H}_{15}\text{Li}$	$\text{Sn}^*\text{C}_{16}\text{H}_{44}\text{Si}_4$
$\text{Sn}^*\text{C}_8\text{H}_{18}$	$\text{Sn}^*\text{C}_{17}\text{H}_{20}\text{S}$
$\text{Sn}^*\text{C}_8\text{H}_{18}\text{Na}_2$	$\text{Sn}^*\text{C}_{17}\text{H}_{36}\text{OS}$
$\text{Sn}^*\text{C}_8\text{H}_{20}$	$\text{Sn}^*\text{C}_{17}\text{H}_{38}\text{Li}_2\text{O}$
$\text{Sn}^*\text{C}_8\text{H}_{20}\text{Hg}$	$\text{Sn}^*\text{C}_{17}\text{H}_{38}\text{O}_2$
$\text{Sn}^*\text{C}_8\text{H}_{20}\text{O}_4$	$\text{Sn}^*\text{C}_{17}\text{H}_{38}\text{Si}$
$\text{Sn}^*\text{C}_9\text{H}_{20}$	$\text{Sn}^*\text{C}_{18}\text{BrF}_{15}$
$\text{Sn}^*\text{C}_9\text{H}_{21}\text{Li}$	$\text{Sn}^*\text{C}_{18}\text{HF}_{15}$
$\text{Sn}^*\text{C}_9\text{H}_{21}\text{Na}$	$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{AuCl}_3\text{P}$

$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{Br}$	$\text{Sn}^*\text{C}_{36}\text{H}_{30}\text{Au}_2\text{I}_2\text{P}_2$
$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{CdCl}$	$\text{Sn}^*\text{C}_{37}\text{H}_{30}\text{Cl}_2\text{Pb}$
$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{Cl}$	$\text{Sn}^*\text{C}_{37}\text{H}_{37}\text{N}$
$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{ClHg}$	$\text{Sn}^*\text{C}_{39}\text{H}_{30}\text{CoLi}$
$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{K}$	$\text{Sn}^*\text{C}_{54}\text{H}_{45}\text{AgCl}_3\text{P}_3$
$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{Li}$	$\text{Sn}^*\text{C}_{54}\text{H}_{45}\text{AuCl}_3\text{P}_3$
$\text{Sn}^*\text{C}_{18}\text{H}_{15}\text{Na}$	$\text{Sn}^*\text{C}_{54}\text{H}_{45}\text{Cl}_3\text{CuP}_3$
$\text{Sn}^*\text{C}_{18}\text{H}_{16}$	$\text{Sn}^*\text{C}_{72}\text{H}_{60}\text{Au}_4\text{Cl}_3\text{P}_4$
$\text{Sn}^*\text{C}_{18}\text{H}_{33}\text{Na}$	$\text{Sn}^*\text{Cl}_2$
$\text{Sn}^*\text{C}_{18}\text{H}_{36}\text{O}$	$\text{Sn}^*\text{Cl}_4$
$\text{Sn}^*\text{C}_{18}\text{H}_{39}\text{N}$	$\text{Sn}^*\text{Cs}$
$\text{Sn}^*\text{C}_{18}\text{H}_{40}\text{O}_2$	$\text{Sn}^*\text{Cu}_3$
$\text{Sn}^*\text{C}_{19}\text{H}_{17}\text{Li}$	$\text{Sn}^*\text{H}_2\text{Na}_2$
$\text{Sn}^*\text{C}_{20}\text{H}_{17}\text{Li}$	$\text{Sn}^*\text{H}_3\text{Na}$
$\text{Sn}^*\text{C}_{20}\text{H}_{18}$	$\text{Sn}^*\text{H}_4$
$\text{Sn}^*\text{C}_{20}\text{H}_{40}\text{O}_2$	$\text{Sn}^*\text{K}$
$\text{Sn}^*\text{C}_{20}\text{H}_{44}\text{O}$	$\text{Sn}^*\text{K}_2$
$\text{Sn}^*\text{C}_{21}\text{H}_{20}$	$\text{Sn}^*\text{Li}$
$\text{Sn}^*\text{C}_{21}\text{H}_{20}\text{O}$	$\text{Sn}^*\text{Li}_2$
$\text{Sn}^*\text{C}_{21}\text{H}_{21}\text{Br}$	$\text{Sn}^*\text{Li}_4$
$\text{Sn}^*\text{C}_{21}\text{H}_{21}\text{Cl}$	$\text{Sn}^*\text{Na}$
$\text{Sn}^*\text{C}_{21}\text{H}_{21}\text{Li}$	$\text{Sn}^*\text{Na}_2$
$\text{Sn}^*\text{C}_{21}\text{H}_{37}\text{N}$	$\text{Sn}^*\text{Na}_3$
$\text{Sn}^*\text{C}_{21}\text{H}_{39}\text{N}$	$\text{Sn}^*\text{Na}_4$
$\text{Sn}^*\text{C}_{21}\text{H}_{40}\text{O}_3$	$\text{Sn}^*\text{Rb}$
$\text{Sn}^*\text{C}_{21}\text{H}_{44}\text{O}$	$\text{SnZn}^*\text{C}_{13}\text{H}_{13}\text{Cl}$
$\text{Sn}^*\text{C}_{22}\text{H}_{22}$	$\text{SnZn}^*\text{C}_{18}\text{H}_{15}\text{Cl}$
$\text{Sn}^*\text{C}_{22}\text{H}_{22}\text{O}$	$\text{Sn}_2^*\text{Au}$
$\text{Sn}^*\text{C}_{22}\text{H}_{48}\text{O}_2$	$\text{Sn}_2^*\text{C}_5\text{H}_{15}\text{Li}$
$\text{Sn}^*\text{C}_{23}\text{H}_{24}\text{S}$	$\text{Sn}_2^*\text{C}_6\text{H}_{18}$
$\text{Sn}^*\text{C}_{23}\text{H}_{26}\text{Si}$	$\text{Sn}_2^*\text{C}_6\text{H}_{18}\text{Hg}$
$\text{Sn}^*\text{C}_{23}\text{H}_{36}$	$\text{Sn}_2^*\text{C}_7\text{H}_{18}\text{BrCl}$
$\text{Sn}^*\text{C}_{23}\text{H}_{42}\text{O}_2$	$\text{Sn}_2^*\text{C}_7\text{H}_{18}\text{Br}_2$
$\text{Sn}^*\text{C}_{23}\text{H}_{48}\text{O}_2$	$\text{Sn}_2^*\text{C}_7\text{H}_{18}\text{Cl}_2$
$\text{Sn}^*\text{C}_{23}\text{H}_{50}\text{OSi}$	$\text{Sn}_2^*\text{C}_7\text{H}_{20}$
$\text{Sn}^*\text{C}_{23}\text{H}_{50}\text{O}_2$	$\text{Sn}_2^*\text{C}_{11}\text{H}_{24}$
$\text{Sn}^*\text{C}_{24}\text{H}_{20}$	$\text{Sn}_2^*\text{C}_{12}\text{H}_{18}$
$\text{Sn}^*\text{C}_{24}\text{H}_{44}\text{O}_2$	$\text{Sn}_2^*\text{C}_{12}\text{H}_{22}$
$\text{Sn}^*\text{C}_{24}\text{H}_{44}\text{O}_3$	$\text{Sn}_2^*\text{C}_{12}\text{H}_{30}$
$\text{Sn}^*\text{C}_{24}\text{H}_{48}\text{OSi}$	$\text{Sn}_2^*\text{C}_{12}\text{H}_{30}\text{Hg}$
$\text{Sn}^*\text{C}_{24}\text{H}_{52}\text{OSi}$	$\text{Sn}_2^*\text{C}_{15}\text{H}_{35}\text{Li}$
$\text{Sn}^*\text{C}_{25}\text{H}_{22}$	$\text{Sn}_2^*\text{C}_{18}\text{H}_{42}\text{Hg}$
$\text{Sn}^*\text{C}_{26}\text{H}_{24}\text{S}$	$\text{Sn}_2^*\text{C}_{24}\text{H}_{30}$
$\text{Sn}^*\text{C}_{30}\text{H}_{26}\text{Fe}$	$\text{Sn}_2^*\text{C}_{24}\text{H}_{54}$
$\text{Sn}^*\text{C}_{30}\text{H}_{40}$	$\text{Sn}_2^*\text{C}_{24}\text{H}_{54}\text{Hg}$
$\text{Sn}^*\text{C}_{30}\text{H}_{54}\text{O}_2$	$\text{Sn}_2^*\text{C}_{24}\text{H}_{66}\text{CdSi}_6$
$\text{Sn}^*\text{C}_{31}\text{H}_{26}\text{AsLi}$	$\text{Sn}_2^*\text{C}_{24}\text{H}_{66}\text{HgSi}_6$
$\text{Sn}^*\text{C}_{32}\text{H}_{36}\text{O}_4$	$\text{Sn}_2^*\text{C}_{24}\text{H}_{66}\text{OSi}_6$
$\text{Sn}^*\text{C}_{33}\text{H}_{28}$	$\text{Sn}_2^*\text{C}_{26}\text{H}_{56}$
$\text{Sn}^*\text{C}_{35}\text{H}_{33}\text{N}$	$\text{Sn}_2^*\text{C}_{30}\text{H}_{33}\text{F}_{15}\text{Si}_3$
$\text{Sn}^*\text{C}_{36}\text{F}_{30}\text{GeHg}$	$\text{Sn}_2^*\text{C}_{30}\text{H}_{66}\text{Cd}$
$\text{Sn}^*\text{C}_{36}\text{H}_{30}\text{AuCl}_3\text{P}_2$	$\text{Sn}_2^*\text{C}_{30}\text{H}_{66}\text{Hg}$

$\text{Sn}_2^*\text{C}_{36}\text{CdF}_{30}$   
 $\text{Sn}_2^*\text{C}_{36}\text{F}_{30}\text{Hg}$   
 $\text{Sn}_2^*\text{C}_{36}\text{H}_{30}$   
 $\text{Sn}_2^*\text{C}_{36}\text{H}_{30}\text{Cd}$   
 $\text{Sn}_2^*\text{C}_{36}\text{H}_{30}\text{Hg}$   
 $\text{Sn}_2^*\text{C}_{37}\text{H}_{31}\text{Li}$   
 $\text{Sn}_2^*\text{C}_{38}\text{H}_{32}$   
 $\text{Sn}_2^*\text{C}_{57}\text{H}_{45}\text{Co}$   
 $\text{Sn}_2^*\text{C}_{60}\text{H}_{68}\text{Hg}$   
 $\text{Sn}_2^*\text{C}_{78}\text{H}_{36}\text{F}_{30}\text{HgP}_2\text{Pt}$   
 $\text{Sn}_2^*\text{K}$   
 $\text{Sn}_2^*\text{Li}$   
 $\text{Sn}_2^*\text{Li}_3$   
 $\text{Sn}_2^*\text{Li}_5$   
 $\text{Sn}_2^*\text{Li}_7$   
 $\text{Sn}_2^*\text{Na}$   
 $\text{Sn}_2\text{Zn}^*\text{C}_{26}\text{H}_{26}$   
 $\text{Sn}_2\text{Zn}^*\text{C}_{36}\text{H}_{30}$   
 $\text{Sn}_2\text{Zn}^*\text{C}_{36}\text{H}_{36}\text{N}_2$   
 $\text{Sn}_3^*\text{C}_{55}\text{H}_{46}$   
 $\text{Sn}_3^*\text{Na}$   
 $\text{Sn}_3^*\text{Na}_4$   
 $\text{Sn}_4^*\text{C}_9\text{H}_{27}\text{Li}$   
 $\text{Sn}_4^*\text{C}_{54}\text{H}_{45}\text{Li}$   
 $\text{Sn}_4^*\text{K}$   
 $\text{Sn}_4^*\text{Na}$   
 $\text{Sn}_4^*\text{Na}_{15}$   
 $\text{Sn}_5^*\text{C}_{72}\text{H}_{60}$   
 $\text{Sn}_5^*\text{Li}_2$   
 $\text{Sn}_5^*\text{Li}_{22}$   
 $\text{Sn}_6^*\text{Na}$   
 $\text{Sn}_6^*\text{Na}_4$   
 $\text{SrZn}^*\text{C}_8\text{H}_{20}$   
 $\text{Te}^*\text{C}_7\text{H}_7\text{Li}$   
 $\text{Te}_2^*\text{C}_{13}\text{H}_{11}\text{Li}$   
 $\text{Te}_2^*\text{C}_{13}\text{H}_{12}$   
 $\text{Tl}^*\text{C}_4\text{H}_7\text{O}_2$   
 $\text{Tl}^*\text{C}_5\text{H}_5$   
 $\text{Tl}^*\text{C}_{12}\text{BrF}_{10}$   
 $\text{Tl}^*\text{C}_{12}\text{H}_{33}\text{Ge}_3\text{Si}_3$   
 $\text{Tl}^*\text{C}_{18}\text{H}_{45}\text{Ge}_3$   
 $\text{Tl}^*\text{C}_{36}\text{H}_{99}\text{Si}_3$   
 $\text{V}^*\text{C}_{10}\text{H}_{10}$   
 $\text{W}^*\text{C}_{21}\text{H}_{15}\text{LiO}_4\text{S}$   
**Zn**

Zn

Reaction with RX: 5.7.2.2.1  
 Reaction with  $\text{R}_2\text{Hg}$ : 5.7.2.2.2  
 Reaction with  $\text{R}_3\text{GeH}$ : 5.7.4.2  
 Reaction with  $\text{R}_3\text{PbX}$ ,  $\text{R}_2\text{PbX}_2$ : 5.7.6.2  
 Reaction with  $\text{R}_3\text{SnX}$ ,  $\text{R}_2\text{SnX}_2$ ,  $\text{RSnX}_3$ :  
 5.7.5.1.1

Reaction with  $(\text{RO})_2\text{SO}_2$ : 5.7.2.2.1

Reducing agent: 5.7.6.1.2

$\text{Zn}^*\text{CH}_2\text{I}_2$   
 $\text{Zn}^*\text{CH}_3\text{ClO}$   
 $\text{Zn}^*\text{C}_2\text{Cl}_3\text{F}_3$   
 $\text{Zn}^*\text{C}_2\text{H}_4\text{Cl}_2$   
 $\text{Zn}^*\text{C}_2\text{H}_4\text{D}_2$   
 $\text{Zn}^*\text{C}_2\text{H}_4\text{I}_2$   
 $\text{Zn}^*\text{C}_2\text{H}_5\text{Cl}$   
 $\text{Zn}^*\text{C}_2\text{H}_5\text{I}$   
 $\text{Zn}^*\text{C}_2\text{H}_6$   
 $\text{Zn}^*\text{C}_2\text{H}_6\text{O}_2$   
 $\text{Zn}^*\text{C}_3\text{F}_7\text{I}$   
 $\text{Zn}^*\text{C}_3\text{H}_3\text{Br}$   
 $\text{Zn}^*\text{C}_3\text{H}_5\text{Br}$   
 $\text{Zn}^*\text{C}_4\text{Cl}_4\text{F}_6$   
 $\text{Zn}^*\text{C}_4\text{H}_6$   
 $\text{Zn}^*\text{C}_4\text{H}_7\text{Cl}$   
 $\text{Zn}^*\text{C}_4\text{H}_{10}$   
 $\text{Zn}^*\text{C}_4\text{H}_{10}\text{O}_4\text{S}$   
 $\text{Zn}^*\text{C}_4\text{H}_{12}\text{Li}_2$   
 $\text{Zn}^*\text{C}_5\text{H}_{10}\text{O}$   
 $\text{Zn}^*\text{C}_6\text{BrF}_5$   
 $\text{Zn}^*\text{C}_6\text{ClF}_5$   
 $\text{Zn}^*\text{C}_6\text{H}_5\text{Br}$   
 $\text{Zn}^*\text{C}_6\text{H}_6$   
 $\text{Zn}^*\text{C}_6\text{H}_{10}$   
 $\text{Zn}^*\text{C}_6\text{H}_{11}\text{Br}$   
 $\text{Zn}^*\text{C}_6\text{H}_{12}\text{BrNO}$   
 $\text{Zn}^*\text{C}_6\text{H}_{14}$   
 $\text{Zn}^*\text{C}_7\text{H}_7\text{Br}$   
 $\text{Zn}^*\text{C}_7\text{H}_7\text{Cl}$   
 $\text{Zn}^*\text{C}_7\text{H}_7\text{I}$   
 $\text{Zn}^*\text{C}_8\text{H}_5\text{Cl}$   
 $\text{Zn}^*\text{C}_8\text{H}_{10}\text{N}_4\text{O}_4$   
 $\text{Zn}^*\text{C}_8\text{H}_{14}$   
 $\text{Zn}^*\text{C}_8\text{H}_{16}$   
 $\text{Zn}^*\text{C}_8\text{H}_{18}$   
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 $\text{Zn}^*\text{C}_8\text{H}_{20}\text{Ca}$   
 $\text{Zn}^*\text{C}_8\text{H}_{20}\text{Sr}$   
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 $\text{Zn}^*\text{C}_{12}\text{H}_{10}$   
 $\text{Zn}^*\text{C}_{12}\text{H}_{10}\text{AuCl}$   
 $\text{Zn}^*\text{C}_{12}\text{H}_{30}\text{Si}_2$   
 $\text{Zn}^*\text{C}_{12}\text{H}_{36}\text{N}_2\text{Si}_4$   
 $\text{Zn}^*\text{C}_{13}\text{H}_{13}\text{ClSn}$   
 $\text{Zn}^*\text{C}_{13}\text{H}_{28}\text{Cl}_2\text{F}_3\text{N}$   
 $\text{Zn}^*\text{C}_{13}\text{H}_{31}\text{Cl}_2\text{N}$   
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 $\text{Zn}^*\text{C}_{16}\text{H}_{34}$   
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 $\text{Zn}^*\text{C}_{18}\text{H}_{15}\text{Li}$   
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$\text{Zn}^*\text{C}_{20}\text{H}_{14}$   
 $\text{Zn}^*\text{C}_{20}\text{H}_{54}\text{Si}_6$   
 $\text{Zn}^*\text{C}_{26}\text{H}_{18}$   
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 $\text{Zr}^*\text{C}_{24}\text{F}_{20}$

## Subject Index

This index supplements the compound index and table of contents by providing access to the text by way of methods, techniques, reaction conditions, properties, effects and other phenomena. Reactions of specific bonds and compound classes are noted when they are not accessed by the heading of the section in which they appear.

For multiple entries, additional keywords indicate contexts and thereby avoid the retrieval of information that is irrelevant to the user's need.

Section numbers are used to direct the reader to those positions in the volume where substantial information is to be found.

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