
Inorganic Reactions
and Methods

Volume 10

Inorganic Reactions and Methods

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Inorganic Reactions and Methods

Volume 10

**The Formation of Bonds to
C, Si, Ge, Sn, Pb (Part 2)**

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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.

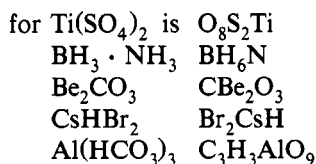
2.5. Author Index

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 BH_6N , Br_2CsH , CBe_2O_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 $\text{H}_3\text{AlO}_9^*\text{C}_3$, $\text{AlO}_9^*\text{C}_3\text{H}_3$ and $\text{O}_9^*\text{C}_3\text{H}_3\text{Al}$. 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 Adurssov 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

The scientific community is appreciative of the JJZ vision for a systematic inorganic chemistry. Many of the contributions had been edited prior to his death; therefore, his precise syntax will remain an important part of the series.

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5. The Formation of Bonds to the Group-IVB Elements (C, Si, Ge, Sn, Pb) (Part 2)

5.3. Formation of Bonds between Elements of Group IVB (C, Si, Ge, Sn, Pb) and Group IIIB (B, Al, Ga, In, Tl)

5.3.1. Introduction

The organometallic chemistry of the group-IIIB elements dominates the discussion of the chemistry of the group-IVB—group-IIIB compounds. Here are found hydroboration, the formation of the carboranes, the industrially important organoaluminums and the synthetically useful organothallium reagents. Combinations involving the lower congeners of group IVB are more rare, some as yet not known. The arrangement of topics has been allowed to reflect this situation.

(J. J. ZUCKERMAN, ED.)

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.1. Industrial Preparation of Boron Carbide

Many proposed formulas are not confirmed. Boron carbide, B_4C , belongs to the family of interstitial compounds of α -rhombohedral boron¹: B_4Si , $B_{12}P_2$, $B_{12}As_2$, $B_{12}O_2$, $B_{12}S$. In the boron-carbon phase diagram, the rhombohedral boron carbide phase exists in the homogeneity range $B_{4.0}C$ (20.0 at % C) to $B_{10.4}C$ (8.8 at % C); boron carbide melts congruently and forms a eutectic between $B_{4.0}C$ and graphite; for the boron-rich compounds a peritectic transformation with a solid solution of carbon in the β -rhombohedral boron structure is assumed²⁻⁴.

Reviews are concerned with structures, properties, preparations⁵⁻¹⁰ and applications.¹¹⁻¹⁵ The boron carbide phase is a complex solid solution.^{4,16}

(F. THÉVENOT)

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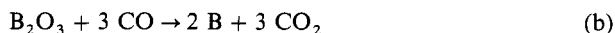
5.3.2.1.1. Industrial Preparation of Boron—Carbide Powders.

Thermodynamic data for synthetic reactions are available¹.

(i) Reduction of Boron Anhydride (or Acid) with Carbon. The overall reaction is written:



The process takes place in two stages:

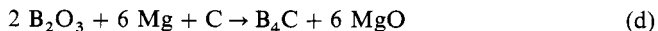


The reduction of B_2O_3 by CO starts at 1673 K.

Brickets of the B_2O_3 -carbon mixture are placed in an electric-arc furnace². The central zone reaches 2473–2773 K and gives a carbide of composition near $\text{B}_{4.3}\text{C}$ containing a few % free graphite. The melted carbide is then crushed. The outer zones of the furnace are less hot (2473–1473 K) and contain unreacted products, which must be recycled.

When a graphite-tube furnace is used at 1973–2073 K under a protective atmosphere, a stoichiometric, fine-grained boron carbide (0.5–5 μm) is obtained. The disadvantage of this method compared with arc melting is its low productivity. It is also possible to use aq ethylene glycol solutions of sugar as the carbon source. In this case, intermediate drying and firing are needed to generate carbon³.

(ii) Reduction of Boron Anhydride with Mg in the Presence of Carbon Black^{4,5}. The reaction is:



A furnace can be used at 1273–1473 K or directly after initiating by a point ignition⁴; likewise, an electric furnace can be used with graphite electrodes under H_2 at 2073 K. To eliminate magnesia, borides ($\text{MgB}_2 \dots$) and unreacted Mg metal, the final product is washed with H_2SO_4 or HCl, then with hot H_2O . A stoichiometric carbide with low granularity (i.e., 0.1–5 μm , with a maximum at 1.4 μm) is obtained. It is possible to prepare graphite-free material; in other cases, it contains 2% graphite.

A soluble carbohydrate that decomposes to carbon may be used with the carbon black⁶.

5.3. Formation of Bonds

3

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.1. Industrial Preparation of Boron Carbide

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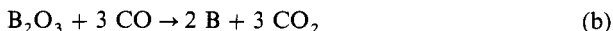
5.3.2.1.1. Industrial Preparation of Boron—Carbide Powders.

Thermodynamic data for synthetic reactions are available¹.

(i) Reduction of Boron Anhydride (or Acid) with Carbon. The overall reaction is written:



The process takes place in two stages:

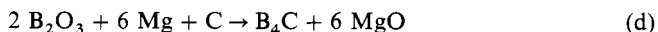


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A soluble carbohydrate that decomposes to carbon may be used with the carbon black⁶.

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3. G. L. Harris, D. S. Parsons, US Pat. 3,885,022 (1975); *Chem. Abstr.*, 83, 62,966 (1975).
4. E. Gray, UK Pat. 6 87,946 (1950); *Doctoral Thesis, No. 1076*, Univ. Geneva, 1945.
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5.3.2.1.2. Densification of Powders.

(i) Natural Sintering. Boron carbide is obtained as powders. The production of pure and dense materials is difficult. Boron carbide possesses strong bonding, low plasticity, high resistance to grain-boundary sliding and low superficial tension in the solid state, all factors that hinder sintering¹. Sintering parameters under an inert atmosphere are known for a wide phase homogeneity range^{2,3}, $B_{8.3}C$ – $B_{4.1}C$. The conditions for dense products are:

1. Boron carbide powders are preferred (reaction sintering gives porous material).
2. The grain size must be as low as possible: $< 3 \mu m$ (powders with sizes greater than $8 \mu m$ cannot be sintered).
3. Higher temperatures (2523–2553 K), near the boron carbide mp (2573–2623 K), are needed.

During sintering, recrystallization starts at 2073 K, and at > 2273 K grains grow rapidly. The resulting twinning can be removed by high-T annealing^{4,5}. The impurity-induced activation of the sintering of industrial B_4C arises from the formation of low-mp borides⁶; the impurities evaporate during sintering⁷.

For sintering at < 2073 K, the addition of metals (Cr, Co, Ni)⁸, glass (at 1623 K), or alumina (at 1373 K) does not enable densities greater than 78 % of the theoretical density (2.52 g cm^{-3}) to be obtained⁹.

For higher T (2423–2523 K), addition of Si, Al, Mg, TiB_2 , or CrB_2 (5–10 wt %)¹⁰, SiC ¹¹, Be_2C ¹², $SiC + Al$ ¹³, improve densification; but exaggerated grain growth, low mechanical strength, and high impurity content not allowed in the nuclear industry prove that this additive process is not satisfactory.

The addition of free graphite yields fine-grained compounds near the theoretical density (94–100 %)^{14–25}. Carbon is better added by the in-situ pyrolysis of a phenolformaldehyde resin ($\approx 9 \text{ wt } \%$)^{15,16,20–25}. Pressure-less sintering of boron-carbide is now possible in industry.

Boron and carbon¹⁹, or boron and silicon ($\leq 20 \text{ at Si } \%$)^{26,27} powders are used as additives.

Organic precursors can be used: both polycarbosilane and a small amount of phenolic resin, giving CSi and carbon by in situ pyrolysis; the resulting boron-carbide ceramics have high density ($> 92 \%$) and contain no free carbon and a small amount of SiC ($\approx 5 \text{ wt } \%$)^{20,28}.

Porous boron-carbide pellets useful in control rods for nuclear reactors are obtained by using organic precursors (furfuryl alcohol and maleic anhydride)²⁹, or a bimodal particle-size distribution of B_4C powders³⁰, or 40 wt % Al addition³¹.

(ii) Hot Pressing of Stoichiometric B_4C (20 at carbon %). Hot pressing is used industrially to prepare different shapes, a great advantage, because boron carbide is hard

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and can be machined only using diamond rectification or diamond or cubic BN lapping^{32–34}. Bonding of segments of boron carbide is possible by this technique^{35,36}. The hot-pressing parameters are not known. To obtain dense products under vacuum or inert atmosphere: (1) fine powders ($< 2 \mu\text{m}$), (2) high T (2373–2473 K), (3) pressures of 30–40 MPa and (4) 15–45 min of pressing should be used^{18,37–42}.

Hot reactive pressing is possible^{18,43}. Densification is easier when sintering takes place simultaneously with synthesis, starting from boron and carbon powders⁴⁰.

The sintered sample can interact with the graphite mold^{32,44}.

A common means of facilitating sample removal consists of lining the inside of the graphite mold with: (1) graphite foils^{38,43}, (2) pyrolytic carbon^{8,45}, (3) hexagonal boron nitride^{18,39,45–52}.

Densification by sintering during hot pressing results from three successive mechanisms^{18,39–41}: (1) particle rearrangement, where enclosed porosity is constant and low; (2) plastic flow, leading to the closing of open porosity; or (3) decreases by volume diffusion of the closed porosity by pore elimination at the end of the hot-pressing operation.

The mechanical strength of sintered boron carbide is 15–20% lower than that of hot-pressed samples^{2,3}; this may be owing to intercrystalline defects in the former case, and transcrystalline ones in the latter case.

(iii) Hot Pressing of Boron-Rich Carbides (2273–2373 K, 20–40 MPa, vacuum or inert atmosphere, 30–60 min). The hot pressing of these compounds is a delicate operation. Extensive carbon diffusion takes place from the mold toward the sample, and the sintering of pure boron produces only boron carbide^{47,48,53}. The diffusion diagram in the B–C system is established^{54–56}. Refractory metallic foils (Ta, Mo, W, etc.) can be used for protection^{46–48,53,57}. Diffusion of the Mo barrier is noted (1.3–1.9 wt %) ⁴⁶.

By using a boron–nitride powder barrier (hot pressed or deposited onto graphite mold and punches), it is possible to prepare dense and pure boron and boron-rich phases, especially carbides (between $\text{B}_{10.4}\text{C}$ and B_4C) by hot pressing in graphite dies^{54,55–58}.

Increasing the boron content to the composition B_{13}C_2 facilitates sintering by reducing temperatures necessary and almost doubling the strength⁴⁹.

Using computer-interactive (APL programming language) methods^{59–62}, it is possible to determine the models of densification kinetics of boron carbides.^{55,59,63} The simplest is:

$$\ln Q = \ln Q_0 - \frac{3tP}{4V} \quad (\text{a})$$

where Q is the porosity, P the pressure, t the time and V the viscosity⁶⁴.

Carbon-rich boron carbides have the lowest viscosity and are more easily densified than the boron-rich materials^{55,63}.

(iv) Hot Pressing with Additions. Activating agents include:

1. The pure elements Mg, Al, Si, V, Cr, Fe, Co, Ni^{8–10,38,49,65–68}, e.g., the addition of 0.75–3.8 wt % of Ni, Fe, and Cu deactivates the sintering of B_4C at all temperatures; by contrast, the addition of 10 wt % additives enhances shrinkage in B_4C at 1898–2133 K^{69–71}. Boron carbide is reaction sintered with Si and Ti^{26,27}.
2. The glass and boron nitride compounds⁹; MgO and Al_2O_3 in alcoholic solution⁷²; Al_2O_3 , sodium silicate with $\text{Mg}(\text{NO}_3)_2$ and Fe_2O_3 ^{66,67}; ethyl silicate^{73,76}; MgF_2 or AlF_3 ³⁸.

The addition of 0.75–3.8 wt % AlF_3 deactivates the sintering of B_4C at all temperatures; 10 wt % of AlF_3 , giving $\text{B}_{12}\text{C}_2\text{Al}$ with release of F_2 gas, enhances shrinkage at 2380 K, owing to grain-boundary diffusion^{69,70}.

The use of dopants in hot pressing has different purposes: (1) lowering the densification T (complete densification at 2173^{49,50} or 2023 K^{66,67}); (2) increasing the oxidation and thermal-shock resistance^{65,74}; and (3) hindering grain growth, thus improving mechanical properties^{38,49,50,66,67,72}.

(v) Hot Isostatic Pressing (HIP). This technique gives high-density samples at lower T (1773–1873 K)⁷⁵. Under 500–752⁷⁷ or 889–1780⁷⁸ MPa Ar, HIP can be used to avoid graphite diffusion [cf. (iii) hot pressing of boron-rich carbides] and should permit the preparation of boron-rich carbides⁷⁹ with improved mechanical properties^{27,75}.

(vi) Densification by Explosion⁸⁰.

(F. THÉVENOT)

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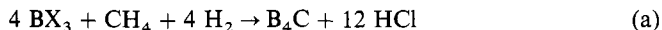
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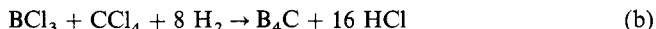
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The reactions are:



with $\text{X} = \text{Cl}^{3-5,8}$ or $\text{Br}^{1,2,7,9,10}$. Single crystals 3–4 mm long are prepared according to¹¹:



Calculations of the equilibrium conditions under which CVD of boron carbide from $\text{BCl}_3\text{--CH}_4\text{--H}_2$ mixtures takes place consider the partial pressures of the gaseous species present. The method minimizes the free energy and the theoretical diagrams are compared to experimental observations¹²⁻¹⁴. Mass-transfer and diffusion kinetics in the gas phase are related to the morphology and composition of the deposits¹⁵⁻¹⁷.

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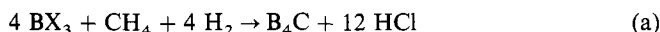
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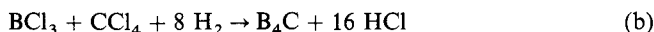
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5.3.2.2.5. by Plasma Synthesis.

Boron carbide can be prepared in a hydrogen-Ar plasma, using: (1) amorphous boron and carbon powders¹, (2) an anode made of a mixture of graphite with boric anhydride (or borax) and a graphite cathode², or (3) a mixture of $\text{BCl}_3\text{--CH}_4$ ^{3–7}. Boron carbide is prepared in excellent yield, a wide stoichiometry range (B:C, 15.8–3.9) and fine spherical granularity (20–30 nm) and characterized by its infrared spectra⁸. The sintering of such a carbide should be promising.

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(F. THÉVENOT)

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5.3. Formation of Bonds

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5.3.2.2. Laboratory Preparation of Boron Carbide

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5.3.2.2.7. Crystal Growth.

Single crystals a few mm long are obtained by chemical vapor deposition (cf. §5.3.2.2.3), or by reduction of B_2O_3 by graphite in an electrical arc^{1,2}. A 6-mm diameter sintered boron carbide rod can be zone melted under Ar³.

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Boron fibers are used to reinforce different epoxy or light-metal matrices. To hinder interactions with metals, they should be protected by boron carbide deposits obtained by chemical vapor deposition.¹ Boron carbide fibers can be prepared directly by reaction of boron obtained by the H_2 reduction of BCl_3 on carbon fibers².

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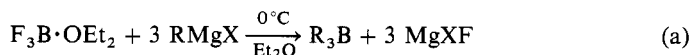
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5.3.2.3.1. by Reaction with More Polar Organometallics (Metal–Metal Exchange, Excluding Amino-, Oxo- and Thio-boron Halides).

The cleavage of metal–carbon bonds by boron halides is used to prepare the organoboranes $R_{3-n}BX_n$ (X = halogen, n = 0, 1, 2)^{1–3}. Although the use of organolithium and organomagnesium-halide reagents is restricted to the preparation of triorganoboranes, the organoderivatives of Zn, Hg, Al, and Si, Ge, Sn and Pb are important in both historic and recent development of the chemistry of the $R_{3-n}BX_n$ compounds.

Symmetrically substituted organoboranes, R_3B , are prepared from $F_3B \cdot OEt_2$ and the corresponding RLi or $RMgX$ compounds^{4–6}. The best yields are obtained by adding the organometallic compound to the $F_3B \cdot OEt_2$, which may be diluted by a hydrocarbon⁷:



Whereas BX_3 (X = Cl, Br, I) can be treated with RLi in hydrocarbon solvents, reactions with $RMgX$ in ethers are not recommended owing to ether cleavage induced by the boron halide.

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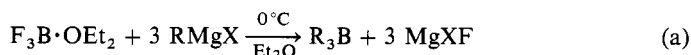
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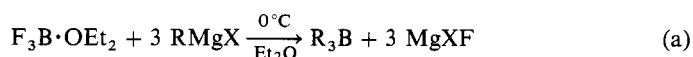
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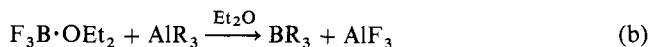
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Organoaluminums, R_3Al , are convenient starting materials for the more volatile organoboranes, R_3B ($R = Me, Et$)^{5,9,10}. Either $F_3B \cdot OEt_2$:



or potassium tetrafluoroborate is used:



One or two carbon-boron bonds are formed by the stoichiometric reaction of BX_3 with organometallic reagents, e.g., see Table 1.

In the laboratory, tetraorganotin compounds are the preferred starting materials for the preparation of RBX_2 and R_2BX ($X = Cl, Br$). In most cases only two of the organo groups are utilized^{1,2,5}:

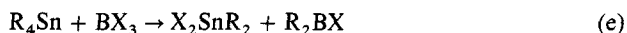
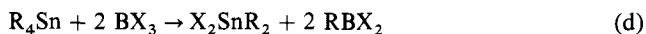
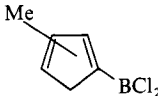
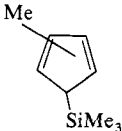
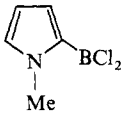
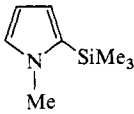
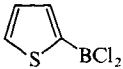
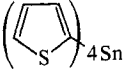
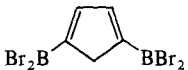
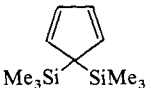


TABLE 1. ORGANOBORON HALIDES FROM METAL-METAL EXCHANGE REACTIONS

Organoboron halides	Organometallic reagents ^{a,b}	Ref.
Fluorides ^c (from BF_3)		
$MeBF_2$	Me_4Sn	17
	Me_2Zn	1
$CH_2=CHBF_2$	$(CH_2=CH)_4Sn$ (52)	18
	$(CH_2=CH)_2Zn$	18
	$(CH_2=CH)_2Hg$	18
$HC\equiv CBF_2$	$HC\equiv CSnMe_3$ (<10)	19
$PhBF_2$	Ph_4Sn	20
	Ph_2Zn	21
Chlorides (from BCl_3)		
$MeBCl_2$	Me_4Sn (>70)	22
	$MeAlCl_2$ (+ BF_3)	23
$EtBCl_2$	Et_4Sn (>70)	22
	Et_3Al	24
	Et_4Pb	11
$CH_2=CHBCl_2$	$(CH_2=CH)_4Sn$ (85)	18,25
	$(CH_2=CH)_2Hg$	25
$cyclo-C_3H_5BCl_2$	$(cyclo-C_3H_5)_4Sn$ (85)	26
	$(cyclo-C_3H_5)_2Hg$	27
	 (10)	28
$PhBCl_2$	Ph_4Sn (56)	29
	Ph_2Hg	30

Organoboron halides	Organometallic reagents ^{a,b}	Ref.
	 (26)	13
	 (78)	13
Me ₂ BCl	Me ₄ Sn	31
Et ₂ BCl	Et ₃ Al (62)	24
(CH ₂ =CH) ₂ BCl	(CH ₂ =CH) ₄ Sn (35)	18
(CF ₂ =CF) ₂ BCl	(CF ₂ =CF) ₂ SnMe ₂ (85)	32
Ph ₂ BCl	Ph ₄ Sn (75)	29
Bromides (from BBr₃)		
MeBBr ₂	(Me ₃ Si) ₂ (93)	33
	Me ₄ Sn (80)	22
EtBBr ₂	Et ₄ Sn (86)	31
	Et ₃ Al (96)	24
CH ₂ =CH—BBr ₂	(CH=CH) ₄ Sn (83)	34
	(CH ₂ =CH) ₂ Hg	25
	 (52)	35
PhBBr ₂	Ph ₄ Sn (69)	31
Me ₂ BBr	Me ₄ Sn (97)	32
Et ₂ BBr	Et ₄ Sn (91)	31
	Et ₃ Al (78)	24
PhMeBBr	Ph ₄ Sn (from MeBBr ₂) (70)	13
Ph ₂ BBr	Ph ₄ Sn (76)	31
Iodides^d (from BI₃)		
MeBI ₂	Me ₄ Sn (66)	31
EtBI ₂	Et ₄ Sn (44)	31
	Et ₃ Al	24
n-BuBI ₂	n-BuLi (84)	8
PhBI ₂	Ph ₄ Sn (59)	31
Me ₂ BI	Me ₄ Sn (72)	31
Et ₂ BI	Et ₄ Sn (66)	31
	Et ₃ Al (63)	24
Ph ₂ BI	Ph ₄ Sn (68)	31

^a The organometallic compound preferred for laboratory syntheses is named first.

^b For recommended reactions, yields (%) are given in parentheses.

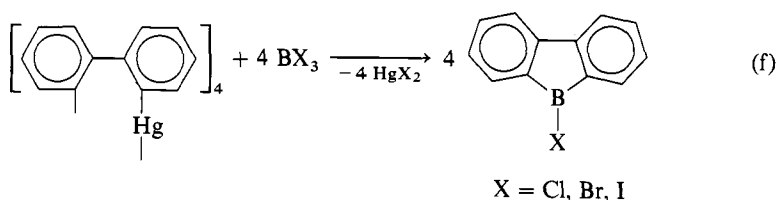
^c Organoboron fluorides are better synthesized by halogen-halogen exchange (e.g., with SbF₃) starting from the organoboron chlorides or bromides.

^d Organoboron iodides can be prepared by halogen-halogen exchange (e.g., with BI₃) starting from the organoboron chlorides.

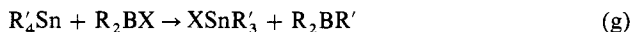
Under severe reaction conditions and with BI_3 , up to four R groups can be abstracted from tin.

Tetraorganolead compounds are also useful in the preparation of RBX_2 and R_2BX . However, there are side reactions (e.g., formation of RX) and mixtures of RBX_2 , R_2BX and R_3B are obtained¹¹.

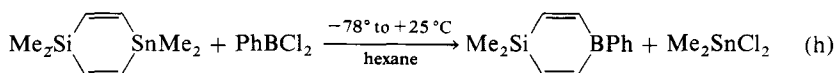
Organomercury and -zinc compounds, R_2Hg , R_2Zn , are no longer of interest for the syntheses of RBX_2 or R_2BX ^{1,2}. In some cases, however, there are organomercurials accessible from which organoboron chlorides can be prepared as shown in the synthesis of 9-borafluorenes¹²:



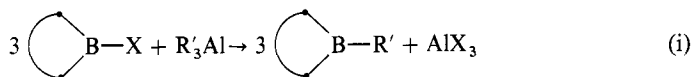
Unsymmetrically substituted, noncyclic¹³ Eq. (g) and cyclic^{14–16} Eq. (h) organoboranes, $\text{R}_2\text{BR}'$ or RBR'_2 , can be prepared by the reaction of organoboron halides with tetraorganotin compounds:



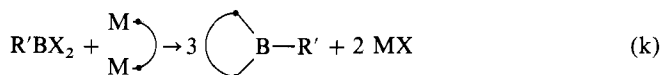
At most two organo groups can be utilized. The reaction¹³ of stannacyclodienes with PhBCl_2 proceeds in most cases in hexane at RT in high yield. The PhBCl_2 attacks the tin–carbon (sp^2) bonds selectively:



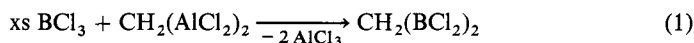
A useful alternative route to cyclic organoboranes, $\text{R}_2\text{BR}'$, is the reaction of cyclic organoboron halides with organoaluminums^{5,9,10,24}:



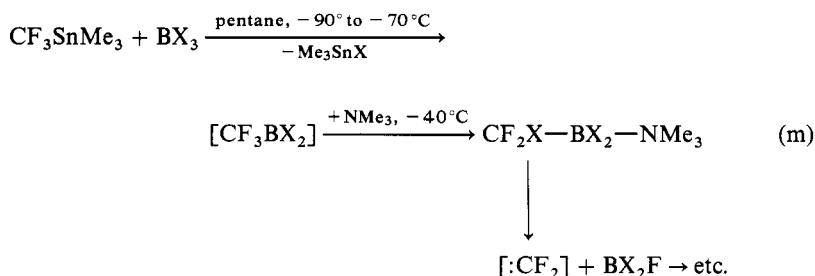
The $\text{R}'_3\text{Al}$ can be substituted by $\text{R}'\text{Li}$ or $\text{R}'\text{MgX}$, although the yields are lower (borate formation, ether cleavage). Moderate yields of cyclic triorganoboranes $\text{R}_2\text{BR}'$ are obtained from the reaction between $\text{R}'\text{BX}_2$ ($\text{X} = \text{F, Cl}$) and dimetallated hydrocarbons ($\text{M} = \text{Li, MgX}$)¹³:



Tetrachlorodiborylmethane is prepared from BCl_3 and $[\text{CH}_2(\text{AlCl}_2)_2]_n$ ³⁷:

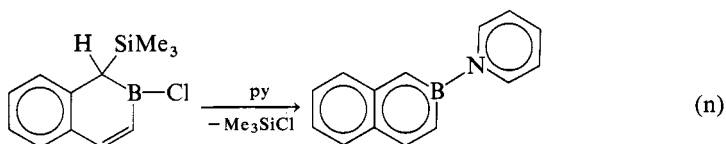


The stannane CF_3SnMe_3 serves as a source for $[\text{CF}_3]^\cdot$ radicals. The intermediacy of unstable $[\text{CF}_3\text{BX}_2]$ is suggested from the isolated adducts $\text{CF}_2\text{X}-\text{BX}_2-\text{NMe}_3$ ³⁸:



where X = F, Cl, Br.

An intramolecular elimination of Me_3SiCl provides a route to 2-boranaphtalene, stabilized as its pyridine (PY) adduct³⁹:



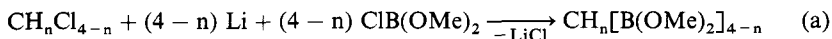
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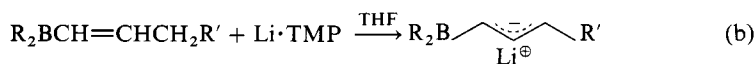
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5.3.2.3.2. by Reaction with an Organoboron-Active-Metal Reagent.

The reaction of CH_2Cl_2 , CHCl_3 and CCl_4 in the presence of Li metal with dimethoxyboron chloride gives access to polyborylated methanes¹:



The reaction involves the formation of carbanions that are stabilized by boryl groups^{2,3}. Similar carbanions are prepared from 9-methyl-9-borabicyclo[3.3.1]nonane (B-methyl-9-BBN)⁴, 9-alkenyl-9-borabicyclo[3.3.1]nonanes (B-alkenyl-9-BBN)⁵, or alkenyldisiamylboranes^{4,5} with 2,2,6,6-tetramethylpiperidine ($\text{Li} \cdot \text{TMP}$) in tetrahydrofuran (THF):



The boron-stabilized allyl carbanions thus formed react with electrophiles.

Borylated carbanions may also be involved in the dehalogenation of ethylboron halides with alkali metals. Mixtures of peralkylated closo- and nido-carbaboranes with 3–7 boron atoms are obtained in low yield from dialkylboron chloride or fluoride, or alkylboron difluoride with Li in THF at -10° and 0°C ^{6,7}.

Dehalogenation of organoboron halides with Na–K alloy in hexane or toluene gives diborylated alkanes⁶, among other products, and for 1-chloroborolane a derivative of 1,3,5-triboracyclohexane is obtained⁸. The reactions of organoboron halides with alkali metals are complex as are further exemplified by the partial elucidation of the composition of the reagent $n\text{-Bu}_2\text{BK}$ which results from di-*n*-butylboron chloride and Na–K alloy in ether.

Methylborylene [MeB], is generated from the reduction of methylboron dibromide with C_8K in boiling benzene^{10–12}. This borylene intermediate adds to double¹⁰ and triple carbon–carbon bonds¹¹, and inserts into C–H bonds of $\text{h}^6\text{-C}_6\text{H}_6\text{Cr(CO)}_3$ and ferrocene¹². However, the intermediacy of [MeB] in the reaction of MeBBr_2 with C_8K in the presence of alkynes is questionable since all the NMR evidence points to haloboration (see §5.3.2.3.4) of the alkynes in the first step followed by various reduction processes¹³.

5.3. Formation of Bonds

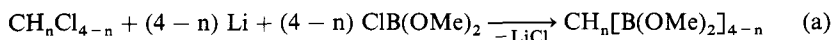
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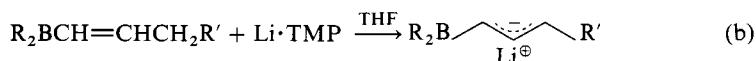
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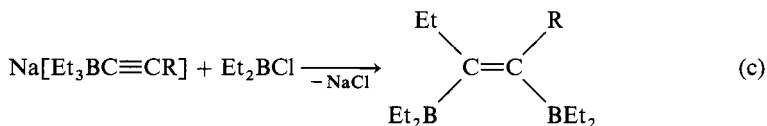
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Alkynyltriethylborates react with dialkylboron halides to form a new boron-carbon bond¹⁴.



The stereoselectivity is remarkable when diethylboron chloride is used as electrophile. With few exceptions¹⁵ the cis-bis(diethylboryl)alkenes are obtained in high yield.

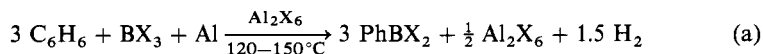
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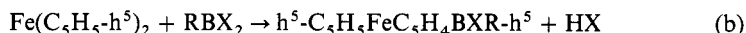
5.3.2.3.3. by Substitution of Hydrocarbons.

The formation of boron-carbon bonds by direct interaction between a hydrocarbon and a boron halide is attractive from the industrial point of view. However, clean reactions are observed in only a few cases¹⁻³.

In the presence of Al metal and catalytic amounts of Al halides, phenylboron dihalides are accessible in good yield (PhBCl_2 , 60–70%)⁴⁻⁷:



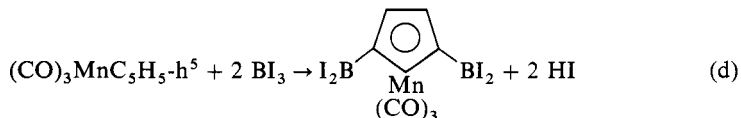
Ferrocene, cymantrene, $\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$, or methylcymantrene are borylated by BBr_3 and BI_3 , MeBI_2 or PhBI_2 in boiling carbon disulfide or cyclohexane to give the metallocenylhaloboranes⁸:



Ferrocene reacts with 2 mol of BBr_3 or BI_3 to give 1,1-bis(dihalogenboryl)ferrocenes:



and cymantrene reacts with 2 mol of BI_3 to give 1,3-bis(diiodoboryl)cymantrene⁹:



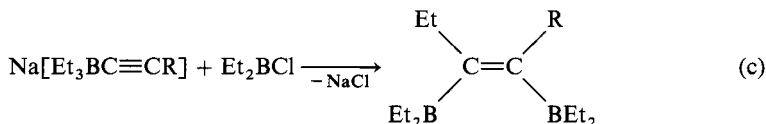
5.3. Formation of Bonds

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5.3.2. Formation of Carbon—Boron Bonds

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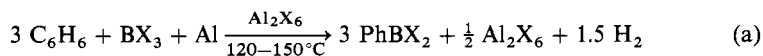
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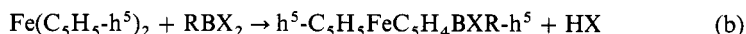
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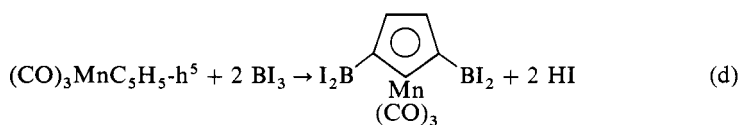
Ferrocene, cymantrene, $\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$, or methylcymantrene are borylated by BBR_3 and BI_3 , MeBI_2 or PhBI_2 in boiling carbon disulfide or cyclohexane to give the metallocenylhaloboranes⁸:



Ferrocene reacts with 2 mol of BBR_3 or BI_3 to give 1,1-bis(dihalogenboryl)ferrocenes:

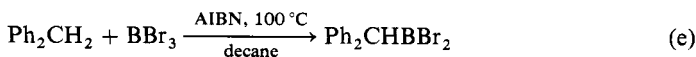


and cymantrene reacts with 2 mol of BI_3 to give 1,3-bis(diiodoboryl)cymantrene⁹:

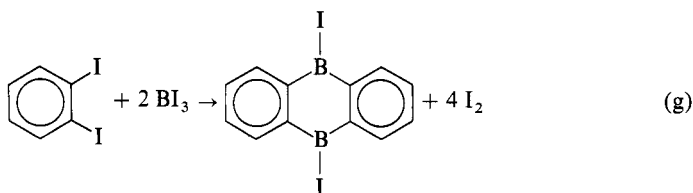


Substituted benzenes and polycyclic aromatic hydrocarbons give mixtures of partly isomerized products^{6,7}. For steric reasons the BX_2 group prefers positions nonadjacent to substituents.

Radical-induced [e.g., by azoisobutyronitrile (AIBN)] substitution of an alkyl group attached to the aromatic ring can occur¹⁰:

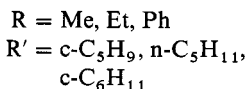


Boron-carbon bonds can be formed by redox reactions between boron iodides and organic iodides, e.g.¹¹⁻¹⁴:



The reactions are carried out by heating the mixtures without solvent to 80–110°C. The I_2 thus formed is removed by sublimation in vacuum and the organoboron iodides are isolated in 50–90% yield.

Transylidation via substitution of a hydrogen atom leads to dialkylboryl-substituted triphenylphosphonium ylides^{15,16}:



(B. WRACKMEYER)

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13. W. Siebert, R. Full, J. Edwin, K. Kinberger, *Chem. Ber.*, **111**, 823 (1978).
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16. H. J. Bestmann, T. Arenz, *Angew. Chem., Int. Ed. Engl.*, **25**, (1986).

5.3. Formation of Bonds

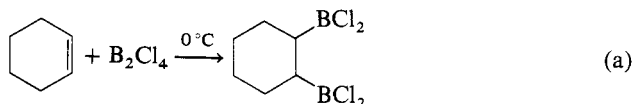
19

5.3.2. Formation of Carbon—Boron Bonds

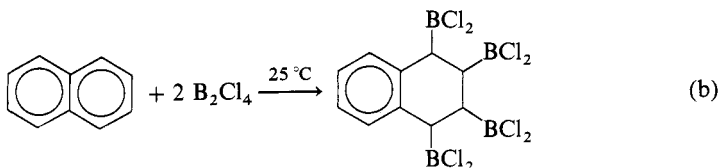
5.3.2.3. from Boron Halides

5.3.2.3.4. by Addition to Olefinic and Acetylenic Linkages (Haloboration).

Addition of boron trihalides to alkenes is popular, although preparative details are frequently omitted. Much of this work should be reinvestigated¹⁻³. The situation is much better for tetrachlorodiborane(4), B_2Cl_4 , which reacts readily with olefins to give diborylated alkanes^{4,5}, e.g., in the cis addition of B_2Cl_4 to cyclohexane⁶:



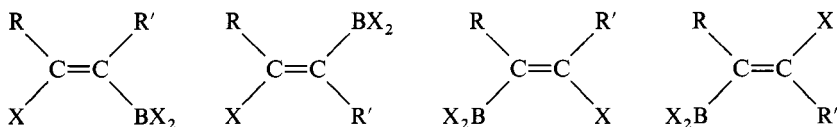
Polycyclic aromatic hydrocarbons react with B_2Cl_4 to give addition products, e.g., with naphthalene⁷:



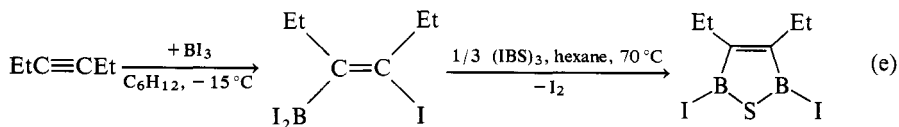
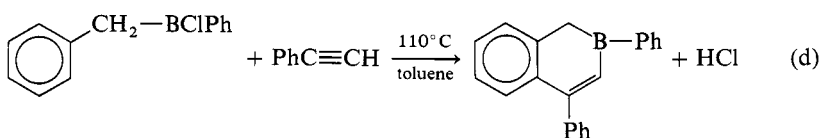
Cyclopropane gives 1,3-addition products⁸ with B_2Cl_4 :



The addition of boron trihalides or organoboron halides to alkynes¹⁻³ can start from alkynes, $RC\equiv CR'$. The 1:1 reaction with BX_3 ($X = Cl, Br, I$) yields the isomers⁹:



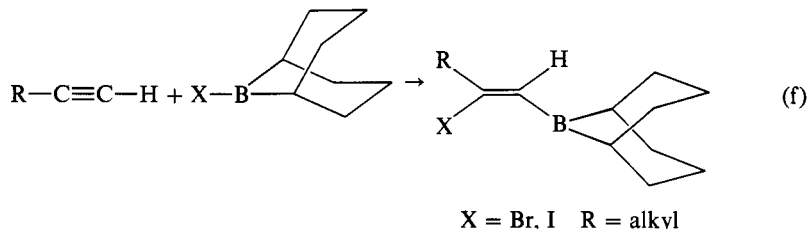
The situation is further complicated when these isomers react with more alkyne. This reaction may then proceed via either transfer of X, or of the alkenyl group. The products⁸ of BX_3 ($X = Cl, Br, I$) with $PhC\equiv CH$ are reformulated from the original assignments¹⁰. The formation of products depends critically on conditions¹¹, which may not always be reproducible, but the addition of boron halides to carbon-carbon triple bonds is an important step to heterocycles^{12,13}, e.g.:



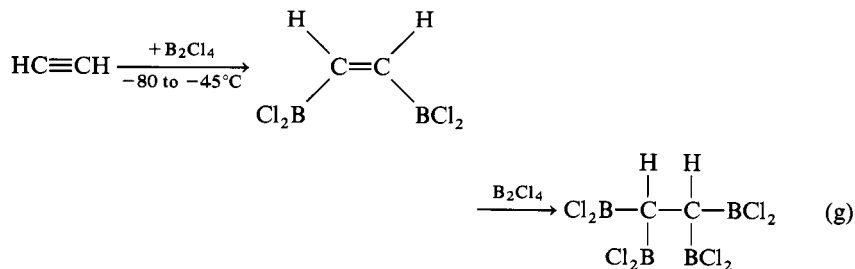
The trans-addition product (trans-3-diiodoboryl-4-iodo-3-hexene) is not shown in Eq. (e), which instead shows an example of the combination of methods to build

boron-carbon bonds. The addition of BI_3 to 3-hexyne is followed by redox (see §5.3.2.3.3) to give the 2,5-diiodothiadiaborolene¹³.

B-bromo- or B-iodo-9-borabicyclo[3.3.1]nonanes add regioselectively to terminal alkynes to give useful intermediates for organic synthesis¹⁴:

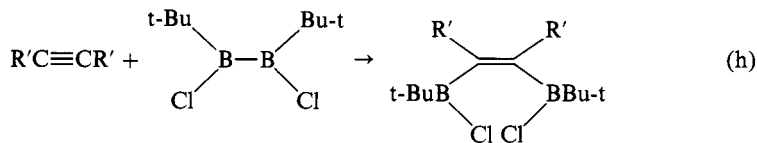


Tetrahalogenodiboranes(4), B_2X_4 , react with ethyne 1:1 ($\text{X} = \text{F}, \text{Cl}$) or 2:1 ($\text{X} = \text{Cl}$). The products are cis-1,2-bis(dihalogenoboryl)ethylene and 1,1,2,2-tetrakis(dichloroboryl)ethane, respectively^{4,5}:



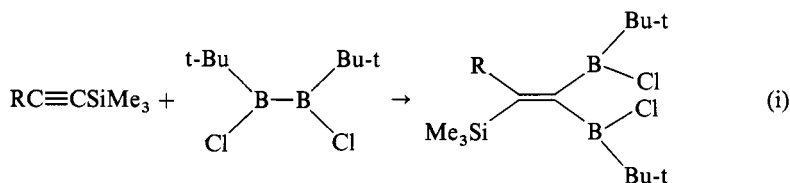
The addition of B_2F_4 to ethyne proceeds sluggishly. Steric hindrance is also important; e.g., B_2Cl_4 with 2-butyne leads to hexamethylbenzene instead of the addition products⁴.

The 1,2-addition to alkynes is also observed with 1,2-di-*t*-butyl-1,2-dichlorodiborane(4)¹⁵:



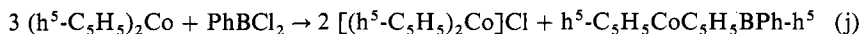
where $\text{R} = \text{R}' = \text{H}, \text{Me}, \text{Et}$.

1,1-Addition occurs with 1-trimethylsilylalkynes¹⁵:



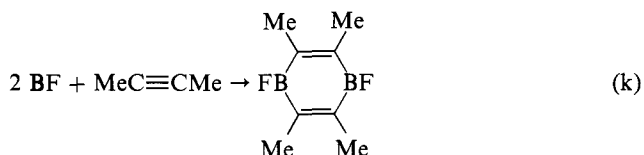
where $\text{R} = \text{Me}, \text{t-BuCH}_2, \text{Ph}, \text{SiMe}_3$.

There are three unique reactions of boron halides with unsaturated systems. The first concerns the ring expansion reaction of di- h^5 -cyclopentadienylcobalt with boron halides¹⁶:

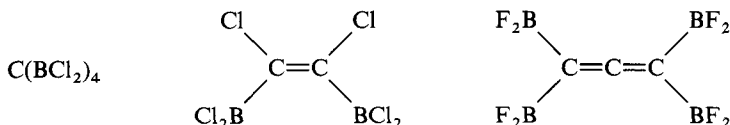


This opens a route to the borabenzene anion, which behaves analogously to the cyclopentadienyl anion¹⁷.

The second is the addition of monomeric BF to alkynes¹⁸. This enables the isolation of a stable derivative of 1,4-diboracyclohexa-2,5-diene:



Finally, the reaction of boron halides with vaporized carbon¹⁹ leads to compounds that are not available by other methods, e.g.:



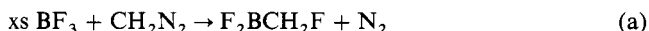
However, the cocondensation of boron halides and carbon vapor yields only ≤ 0.05 g per pass, and no continuous process is available.

(B. WRACKMEYER)

1. R. Köster, *Organobor Verbindungen I*, in *Methoden der Organischen Chemie Houben-Weyl*, R. Köster, ed., Vol. 13/3a, Georg Thieme Verlag, Stuttgart, 1982, p. 378.
2. A. Meller, *Gmelin Handbuch der Anorganischen Chemie*, Vol. 34, Part 9, Springer Verlag, Berlin, 1976, p. 126.
3. A. Pelter, K. Smith, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 3, D. N. Jones, ed., Pergamon Press, New York, 1979, p. 689.
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11. R. J. Binnewirtz, H. Klingenberger, R. Welte, P. Paetzold, *Chem. Ber.*, **116**, 1271 (1983).
12. P. Paetzold, H. G. Smolka, *Chem. Ber.*, **103**, 289 (1970).
13. W. Siebert, R. Full, J. Edwin, K. Kinberger, *Chem. Ber.*, **111**, 823 (1978).
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5.3.2.3.5. by Reaction with Diazoalkanes.

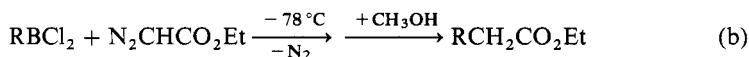
Boron halides with diazomethane leads to polymethylene¹. Polymerization can be suppressed in the presence of BF_3 . The reaction between CH_2N_2 and BF_3 in the gas phase under N_2 at -40°C and 50 torr (6.67×10^3 Pa) yields fluoromethylboron difluoride quantitatively:



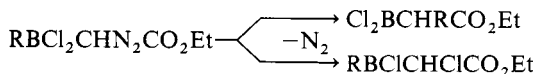
The compound is unstable and cannot be stored in glassware as a liquid².

The mechanism of the polymerization of CH_2N_2 involves transfer of one alkyl group from boron to carbon³ in the reaction between triorganoboranes and diazoalkane derivatives^{4,5}.

This method is improved by using diorganoboron chlorides⁶ and organoboron dichlorides⁷ to react with diazoacetic acid ethyl ester at -78°C . Nitrogen is evolved, and, after addition of methanol (at -78°C), the acetic acid ethyl ester derivative can be isolated in 50–90% yield:



Although no intermediate is isolated or identified, the formation of an adduct may be followed by migration of the R or Cl group to carbon:



Upon methanolysis both possible intermediates are expected to give the same product^{6,7}.

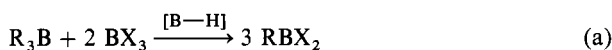
(B. WRACKMEYER)

1. H. Meerwein, *Angew. Chem.*, **60**, 78 (1948).
2. J. Goubeau, R. H. Rohwedder, *Justus Liebigs Ann. Chem.*, **604**, 168 (1957).
3. A. G. Davies, D. G. Hare, O. R. Khan, J. Sikora, *Proc. Chem. Soc. (London)* 172 (1961).
4. J. Hooz, S. Linke, *J. Am. Chem. Soc.*, **90**, 5936 (1968).
5. J. Hooz, S. Linke, *J. Am. Chem. Soc.*, **90**, 6891 (1968).
6. H. C. Brown, M. M. Midland, A. B. Levy, *J. Am. Chem. Soc.*, **94**, 3662 (1972).
7. J. Hooz, J. N. Bridson, J. G. Calzada, H. C. Brown, M. M. Midland, A. B. Levy, *J. Org. Chem.*, **38**, 2574 (1973).

5.3.2.3.6. by Redistribution Reactions with Organoboranes.

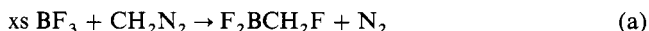
Since triorganoboranes are readily obtained^{1–3}, redistribution between R_3B and boron halides is an important route to organoboron halides. The ligand exchange proceeds at $>100^\circ\text{C}$ in the absence of solvents, and the products are formed according to the stoichiometry employed. The isolation of the organoboron halide requires mild conditions in order to prevent further ligand exchange.

Redistribution is catalyzed by small amounts of alkylidiborane(6) derivatives. The exchange reactions are complete at RT ($\text{R} = \text{alkyl}$), which is convenient for the volatile BX_3 compounds:



5.3.2.3.5. by Reaction with Diazoalkanes.

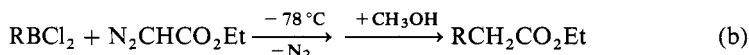
Boron halides with diazomethane leads to polymethylene¹. Polymerization can be suppressed in the presence of BF_3 . The reaction between CH_2N_2 and BF_3 in the gas phase under N_2 at -40°C and 50 torr (6.67×10^3 Pa) yields fluoromethylboron difluoride quantitatively:



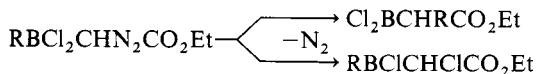
The compound is unstable and cannot be stored in glassware as a liquid².

The mechanism of the polymerization of CH_2N_2 involves transfer of one alkyl group from boron to carbon³ in the reaction between triorganoboranes and diazoalkane derivatives^{4,5}.

This method is improved by using diorganoboron chlorides⁶ and organoboron dichlorides⁷ to react with diazoacetic acid ethyl ester at -78°C . Nitrogen is evolved, and, after addition of methanol (at -78°C), the acetic acid ethyl ester derivative can be isolated in 50–90% yield:



Although no intermediate is isolated or identified, the formation of an adduct may be followed by migration of the R or Cl group to carbon:



Upon methanolysis both possible intermediates are expected to give the same product^{6,7}.

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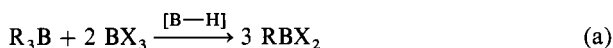
6. H. C. Brown, M. M. Midland, A. B. Levy, *J. Am. Chem. Soc.*, **94**, 3662 (1972).

7. J. Hooz, J. N. Bridson, J. G. Calzada, H. C. Brown, M. M. Midland, A. B. Levy, *J. Org. Chem.*, **38**, 2574 (1973).

5.3.2.3.6. by Redistribution Reactions with Organoboranes.

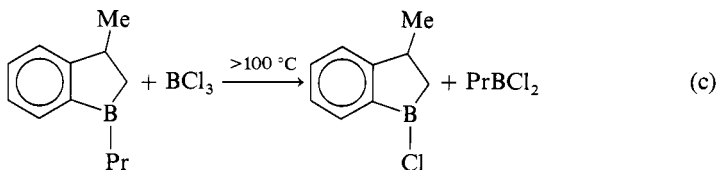
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Redistribution is catalyzed by small amounts of alkyldiborane(6) derivatives. The exchange reactions are complete at RT ($\text{R} = \text{alkyl}$), which is convenient for the volatile BX_3 compounds:



The course of reaction is independent of the source of the catalyst $[B-H]$, as shown for $H_3B \cdot SMe_2$ as a catalyst. Before the organoboron halide can be purified by distillation, the catalyst should be destroyed by adding a small amount of an olefin⁴⁻⁶.

Cyclic organoboron halides can also be prepared by redistribution. This is important when the triorganoborane is not readily available by metal-metal exchange (see §5.3.2.3.1) or in cyclic hydroboration (see §5.3.2.5), e.g., in the preparation of 1-chloroboraindane⁷:



(B. WRACKMEYER)

1. H. C. Brown, G. W. Kramer, A. B. Levy, M. M. Midland, *Organic Synthesis via Boranes*, Wiley-Interscience, New York, 1975.
2. R. Köster, *Organobor Verbindungen I*, in *Methoden der Organischen Chemie* Houben-Weyl, R. Köster, ed., Vol. 13/3a, Georg Thiema Verlag, Stuttgart, 1982, p. 13.
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4. R. Köster, M. Grassberger, *Justus Liebigs Ann. Chem.*, 719; 169 (1968).
5. H. C. Brown, A. B. Levy, *J. Organomet. Chem.*, 44, 233 (1972).
6. R. Köster, P. Binger, *Inorg. Synth.*, 15, 134 (1974).
7. R. Köster, *Adv. Organomet. Chem.*, 2, 257 (1964).

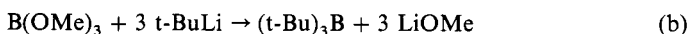
5.3.2.4. from Boron Alkoxides with More-Polar Organometallics

The reaction of boron alkoxides with organometallics to form B—C bonds is the transmetallation process:



where $X = -OR$, halogen, $-NR_2$, $-SR$, $-OB$ $\begin{array}{c} \diagup \\ \diagdown \end{array}$, and $M = \text{a metal}$.

The syntheses of organoboranes by transmetallation is described in monographs and reviews¹⁻⁸, and a compilation of physical data on organoboranes is available⁹. Halogenoboranes and boron alkoxides are the most often used substrates in this transformation; e.g., for the latter, trialkoxyboranes, trialkoxyboroxines, esters of alkyl- and arylboronic and -borinic acids are utilized. The choice between alkoxy- and halogenoboranes depends on the circumstances. However, alkyl group isomerization occurring on the alkylation of halogenoboranes¹⁰⁻¹² can be avoided using boron alkoxides¹²⁻¹⁵:



5.3. Formation of Bonds

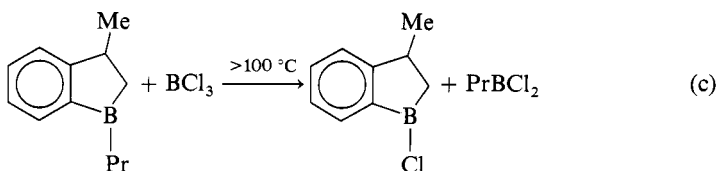
23

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.4. from Boron Alkoxides

The course of reaction is independent of the source of the catalyst $[B-H]$, as shown for $H_3B \cdot SMe_2$ as a catalyst. Before the organoboron halide can be purified by distillation, the catalyst should be destroyed by adding a small amount of an olefin⁴⁻⁶.

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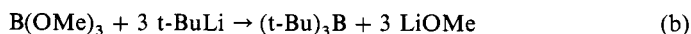
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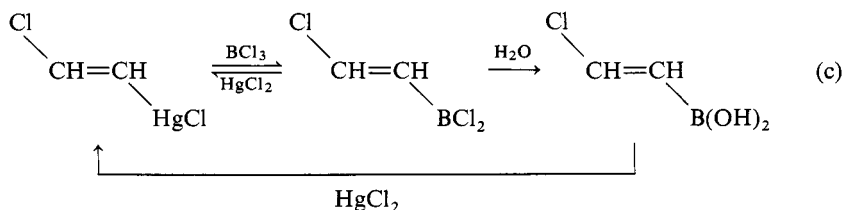


where X = —OR, halogen, —NR₂, —SR, —OB $\begin{array}{c} \diagup \\ \diagdown \end{array}$, and M = a metal.

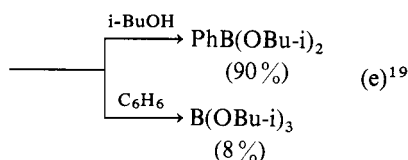
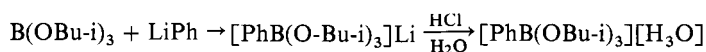
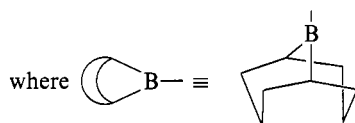
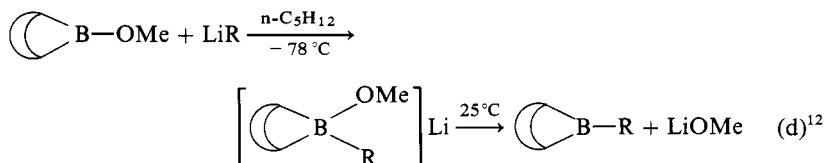
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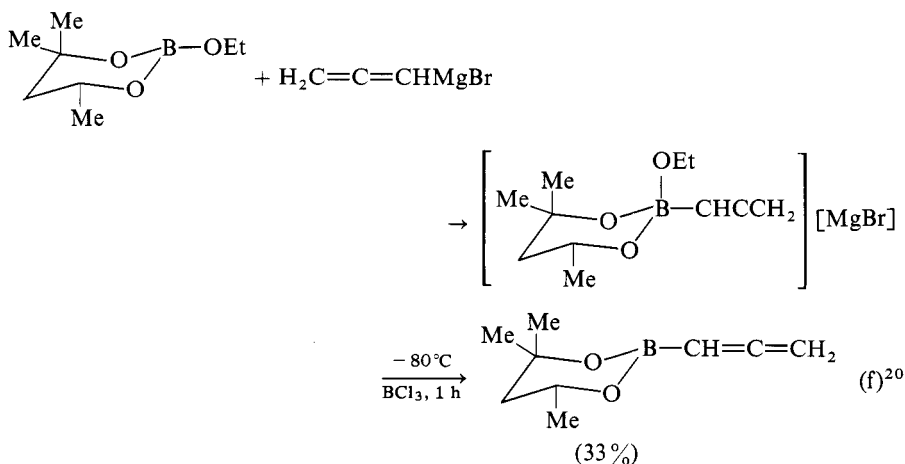


Among the organometallics, organomagnesium-halide reagents, organolithiums and organoaluminums are most frequently used owing to their availability and high reactivity. The reactivity order of phenyl derivatives of Mg and IIB-group metals toward $\text{B}(\text{O}i\text{Bu}-n)_3$ is¹⁶ $\text{Mg} > \text{Cd} > \text{Zn} > \text{Hg}$. Reactions of boron alkoxides with derivatives of the most electropositive metals are most facile. This trend is reflected in the qualitative reactivity order: $\text{K}, \text{Na} > \text{Li} > \text{Mg}, \text{Al} > \text{Cd}, \text{Zn} > \text{Hg}$. With more reactive organometallics, the equilibrium in Eq. (a) shifts to the right. However, to achieve the best yields, one of the products often is removed from the reaction mixture by distillation, precipitation or hydrolysis. The position of equilibrium for organic derivatives of less electropositive metals depends on the nature of the reagents and the conditions. In some cases, transformations in both directions are possible^{17,18}:

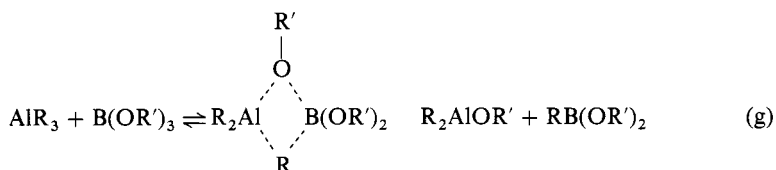


Transmetallations involving boron alkoxides may proceed either via intermediates or by direct substitution. The formation of the intermediate ate complexes is observed with organolithium and RMgX reagents, and they can be isolated^{12,19-21}. These complexes are transformed into product by thermal decomposition¹², by the action of *xs* alkoxyborane²², amines^{23,24}, HCl ^{19,20,25-27} or electron-pair acceptor acids^{20,21,28}, carboxylic acid chlorides^{20,29,30}, or by hydrolysis in the presence of mineral acids:





On the other hand, reaction of alkoxyboranes with organoaluminum compounds proceeds via weakly polar associates and a transition state in which the organic group is bonded to both the boron and the Al atoms³¹:



The reactions of the RMgX and organolithium reagents with boron alkoxides are carried out in ethers or hydrocarbons at low T. The amount of the reagents must be carefully controlled to avoid ate-complex formation between the products and the starting organometallic. Isolation of products requires treatment of the mixtures with dilute mineral acids. However, triarylboranes, benzylic and allylic boranes are hydrolyzed under these conditions. Consequently, care must be taken in isolating such boranes using stoichiometric amounts of acid or working in anhydrous conditions.

Transmetalation is a versatile method for the synthesis of organoboranes, particularly those with aryl, alkynyl and tertiary alkyl groups not available via hydroboration of alkenes. However, the reactivity of organometallics used with boron alkoxides is a limitation in the synthesis of functionalized organoboranes. The catalytic effect of organometallics on redistributions of organoboranes may also be a complicating factor in the case of unsymmetrical organoboranes.

(H. C. BROWN, M. ZAJDLIEWICZ)

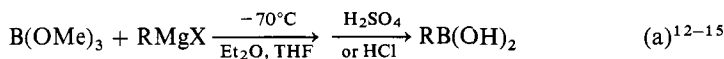
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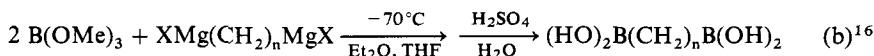
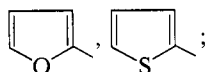
5.3.2.4.1. Alkyl- and Arylboronic Acids.

Several methods are available for the synthesis of boronic acids and their esters^{1,2} (see also refs. 1–8, §5.3.2.4). Trialkoxyboranes react with polar organometallics. Organomagnesium halides and organolithiums are most often used.

The reaction of RMgX reagents with trialkoxyboranes can be controlled to proceed in a stepwise manner. It provides a method for alkyl- and arylboronic acids and their esters. Stoichiometric amounts of reagents or xs trialkoxyborane is used and the reaction is carried out at low T^{1–16}:



where THF is tetrahydrofuran and R = n-Pr—, n-Bu—, i-Bu—, t-Bu—, PhCH₂—,



5.3. Formation of Bonds

5.3.2. Formation of Carbon—Boron Bonds

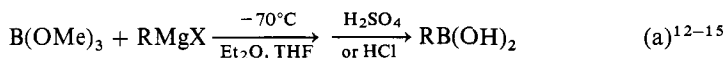
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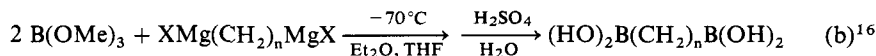
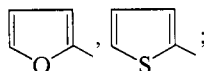
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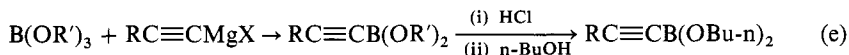
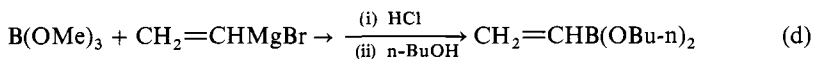
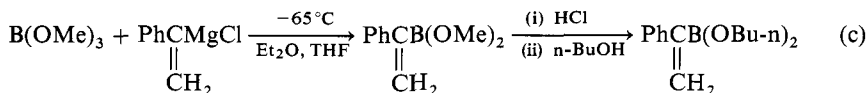
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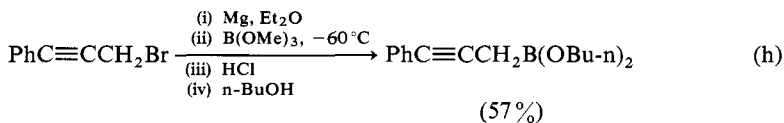
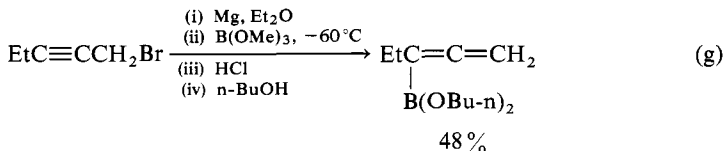
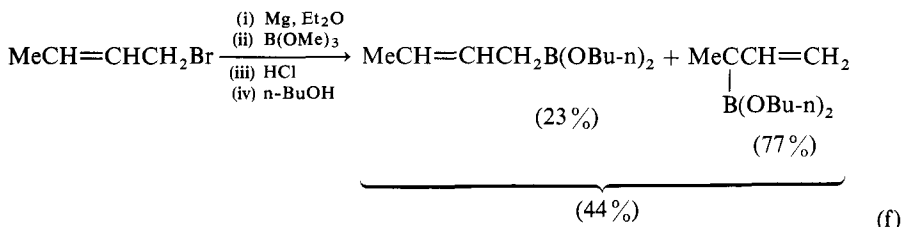


where $n = 4, 5, 6, 10$. Alkenyl¹⁷⁻¹⁹, alkynyl²⁰⁻²², allylic^{23,24}, propargylic and allenic^{4,11} groups can also be attached to boron:

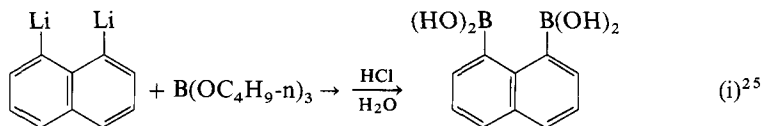


where $\text{R} = \text{H, Me, CH}_2=\text{CH}-$; $\text{R}' = \text{Me, } n\text{-Bu}$.

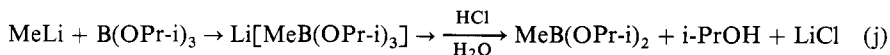
When substituted allylic and propargylic groups are used, rearranged products are often obtained. The extent of rearrangement depends on the substitution at the double or triple bonds. The aliphatic substituents facilitate formation of the allenic products, whereas the opposite is observed for aryl-substituted triple bonds^{4,11}:



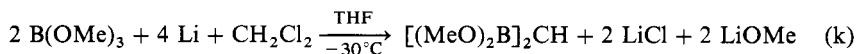
Organolithiums are often applied in the synthesis of arylboronic acids²⁵⁻²⁷ [see also Eq. (e), §5.3.2.4].



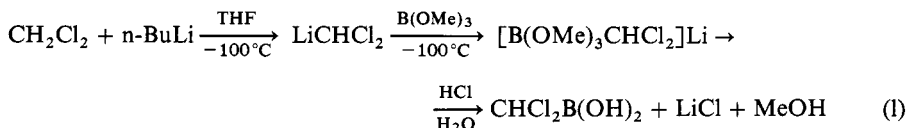
Although lithium alkyls, owing to higher reactivity, show a tendency to form dialkylated products²⁸, they can also be used to prepare certain alkylboronic esters²⁹⁻³¹.



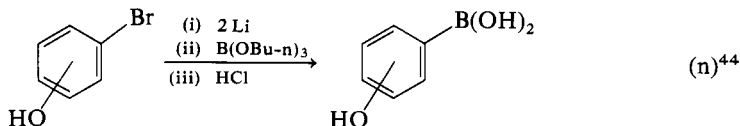
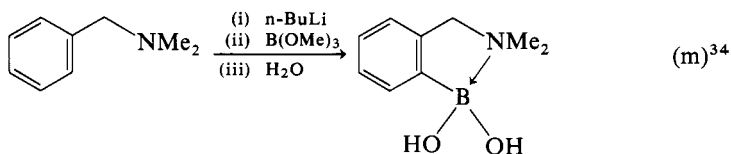
High reactivity of lithium alkyls can be advantageous, *e.g.*, in the synthesis of *gem*-dibora derivatives³²:



or esters of dichloromethylboronic acid³³:



Some functionalized alkyl- and arylboronic acids can be prepared *via* transmetalation³³⁻⁴⁴ [see also Eq. (1)]:



where OH = *m*-, *p*-, *o*- (anhydride). Organoaluminums are used less frequently for preparing alkylboronic acids by transmetalation with boron alkoxides.^{11,45}

(H. C. BROWN, M. ZAJDLIEWICZ)

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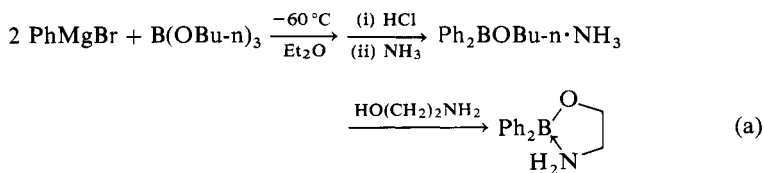
5.3.2. Formation of Carbon—Boron Bonds

5.3.2.4. from Boron Alkoxides with More-Polar Organometallics

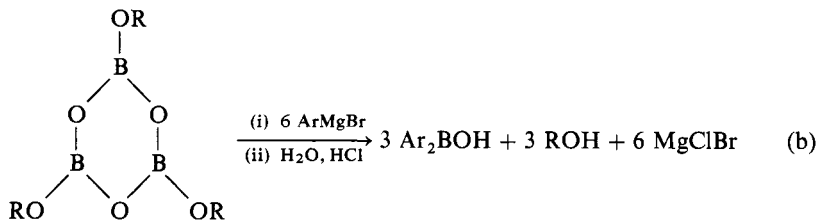
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5.3.2.4.2. Alkyl- and Arylborinic Acids.

Although symmetrical dialkylborinic acids can be obtained from boron alkoxides or boronic esters and organolithium or RMgX reagents¹⁻⁹, these compounds usually are more conveniently synthesized, either by partial hydrolysis of trialkylboranes^{10,11}, or by hydroboration of alkenes with monohalogenoboranes followed by hydrolysis^{12,13} (see also refs. 1-8, §5.3.2.4 and ref. 2, §5.3.2.4.1). Diarylborinic acids are prepared by the reaction of 2 mol of ArMgX with trialkoxyborane at low T^{14,15}. The products are isolated either as esters of simple alcohols or as β -aminoethanol derivatives¹⁶:



Trialkoxyboroxines are convenient starting materials, and their reaction with RMgX reagents can be carried out at RT. The best yields are achieved using a 9:1 ratio of reagents at 25°C, although at stoichiometric ratios the yields are also satisfactory^{17,18}:



5.3. Formation of Bonds

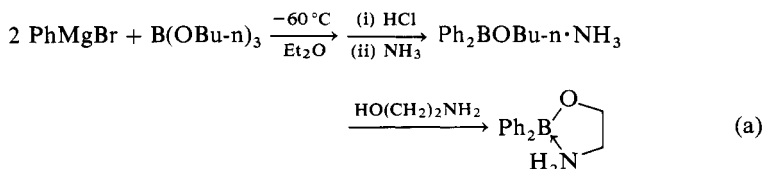
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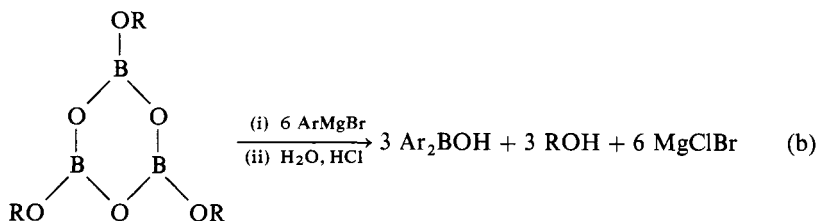
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5.3.2.4.2. Alkyl- and Arylborinic Acids.

Although symmetrical dialkylborinic acids can be obtained from boron alkoxides or boronic esters and organolithium or RMgX reagents¹⁻⁹, these compounds usually are more conveniently synthesized, either by partial hydrolysis of trialkylboranes^{10,11}, or by hydroboration of alkenes with monohalogenoboranes followed by hydrolysis^{12,13} (see also refs. 1-8, §5.3.2.4 and ref. 2, §5.3.2.4.1). Diarylborinic acids are prepared by the reaction of 2 mol of ArMgX with trialkoxyborane at low T ^{14,15}. The products are isolated either as esters of simple alcohols or as β -aminoethanol derivatives¹⁶:



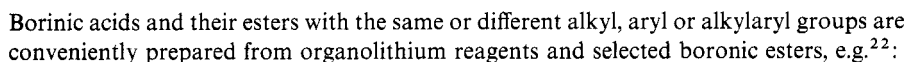
Trialkoxyboroxines are convenient starting materials, and their reaction with RMgX reagents can be carried out at RT. The best yields are achieved using a 9:1 ratio of reagents at 25°C, although at stoichiometric ratios the yields are also satisfactory^{17,18}:

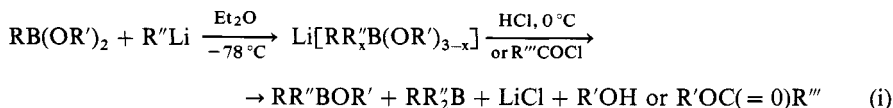
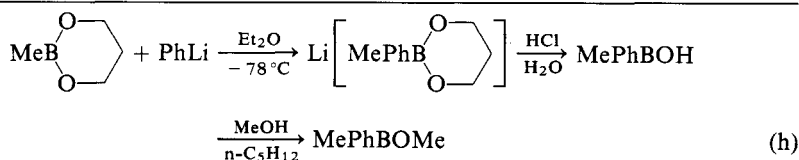


$$\begin{array}{c}
 \text{PhB(Obu-i)}_2 + \text{LiPh} \xrightarrow[\text{C}_6\text{H}_6, 0^\circ\text{C}]{\text{Et}_2\text{O}} [\text{Ph}_2\text{B(Obu-i)}_2]\text{Li} \\
 \downarrow \\
 \begin{array}{ccc}
 \text{dry, HCl} & & \text{H}_2\text{O, HCl} \\
 \downarrow & & \downarrow \\
 [\text{Ph}_2\text{B(Obu-i)}_2]\text{H} & \begin{array}{cc} \xrightarrow{(5\%)} \text{PhB(Obu-i)}_2 & \xleftarrow{(62\%)} \end{array} & [\text{Ph}_2\text{B(Obu-i)}_2][\text{H}_3\text{O}] \\
 & \begin{array}{cc} \xrightarrow{(82\%)} \text{Ph}_2\text{BOBu-i} & \xleftarrow{(28\%)} \end{array} & \\
 \end{array}
 \end{array} \quad (c)^6$$

$$\text{PhB(Obu-i)}_2 + \text{LiR} \xrightarrow[-50^\circ \text{ to } -60^\circ\text{C}]{\text{Et}_2\text{O}} \xrightarrow[\text{dry}]{\text{HCl}} \text{RPhBOBu-i} \quad (56-67\%) \quad (d)^{19}$$
$$\text{RB(OBu-}n\text{)}_2 + \text{R}'\text{Li} \xrightarrow[-70^\circ\text{C}]{\text{Et}_2\text{O}} \xrightarrow[\text{dry}]{\text{HCl}} \text{RR}'\text{BOBu-}n \quad (\text{e})^{7,8}$$

Transmetalation of alkenyl- and alkynylboronic acid esters with ArMgX reagents provides an access to mixed alkenyl-, aryl-, and alkynylboronic acids. In contrast, treatment of alkynylboronic acid esters with alkyl RMgX compounds displaces the alkynyl group and alkylboronic acid ester is formed^{20,21}:





where R = Me, n-Bu, t-Bu, cyclohexyl, Ph; R' = i-Pr; R'' = Ph, i-Pr, t-Bu; R''' = Ph.

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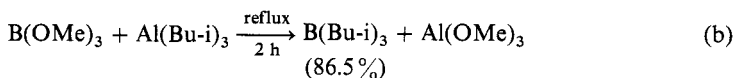
1. R. M. Washburn, F. A. Billig, M. Bloom, M. Albright, E. Levens, in *Borax to Boranes*, D. L. Martin, ed., *Advances in Chemistry Series*, No. 32 American Chemical Society, Washington DC, 1961, p. 208.
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5.3.2.4.3. to form Organoboranes with Three B—C Bonds.

Three alkyl- or aryl groups can be attached to the boron atom via transmetallation of boron alkoxides with reactive organometallics¹⁻⁸ (see also refs. 1-8, §5.3.2.4). Organoboranes were first synthesized in this way⁹:



Organomagnesium-halide, organolithium and organoaluminum reagents are preferred to other organometallics. Commercially available trialkylaluminum compounds are convenient starting materials for the lower trialkylboranes. Solvents are not required, and trialkylborane can be isolated by distillation directly from the mixture¹⁰:

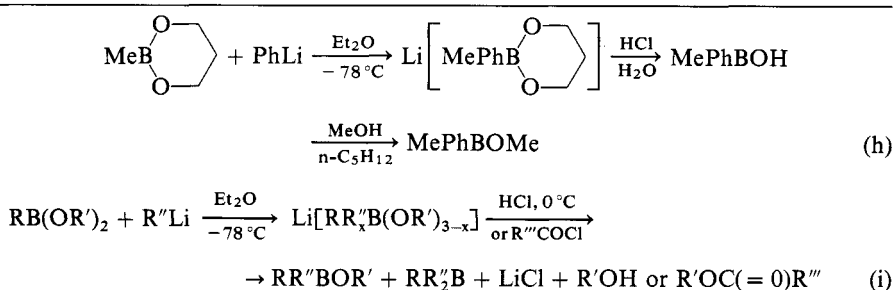


5.3. Formation of Bonds

31

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.4. from Boron Alkoxides with More-Polar Organometallics



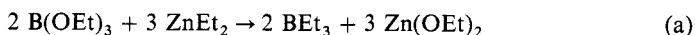
where R = Me, n-Bu, t-Bu, cyclohexyl, Ph; R' = i-Pr; R'' = Ph, i-Pr, t-Bu; R''' = Ph.

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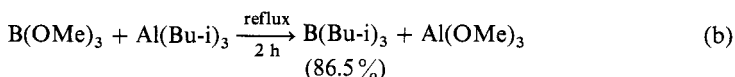
1. R. M. Washburn, F. A. Billig, M. Bloom, M. Albright, E. Levens, in *Borax to Boranes*, D. L. Martin, ed., *Advances in Chemistry Series*, No. 32 American Chemical Society, Washington DC, 1961, p. 208.
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5.3.2.4.3. to form Organoboranes with Three B—C Bonds.

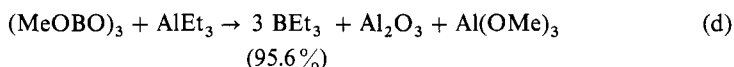
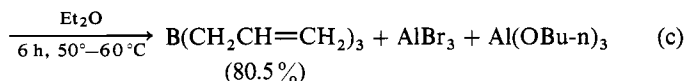
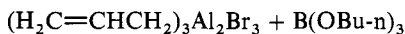
Three alkyl- or aryl groups can be attached to the boron atom via transmetallation of boron alkoxides with reactive organometallics¹⁻⁸ (see also refs. 1-8, §5.3.2.4). Organoboranes were first synthesized in this way⁹:



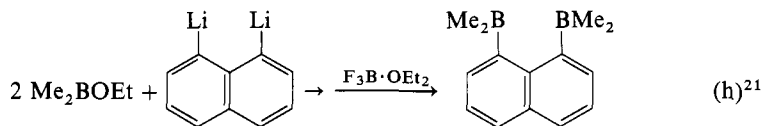
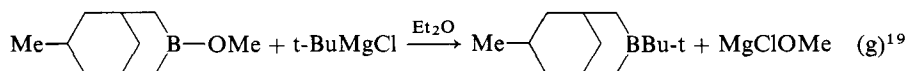
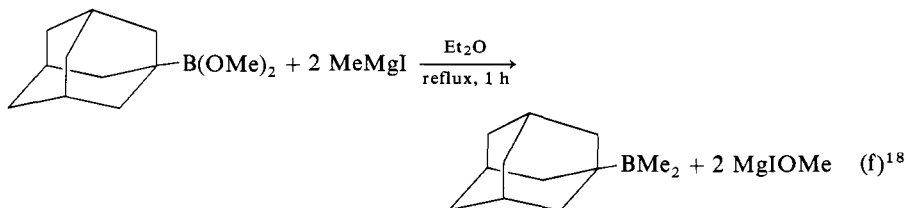
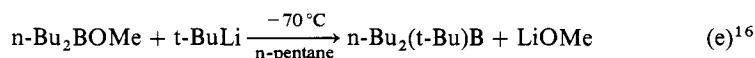
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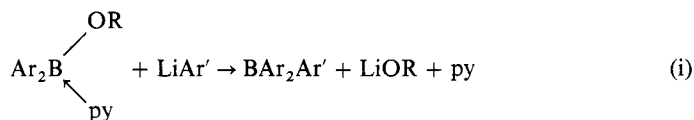
Aluminum sesquihalides^{11–14} or even mixtures of metallic Al, alkyl halide and trialkoxyborane, can also be used¹⁵. Trialkoxyboroxines, from trialkoxyboranes and boron trioxide, are convenient boron substrates^{12,13}:



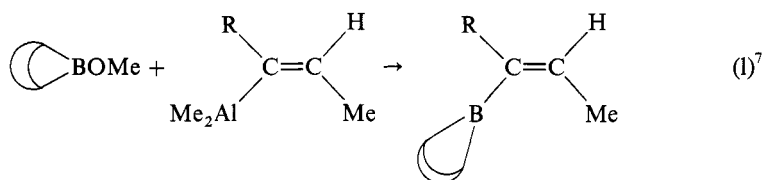
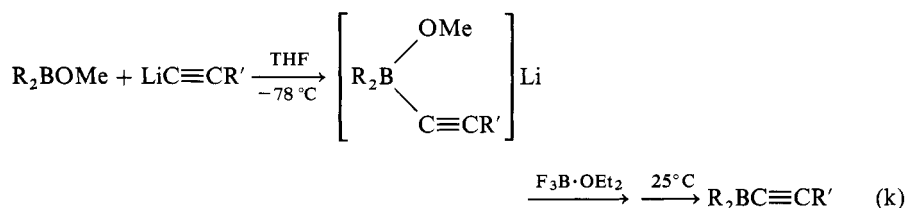
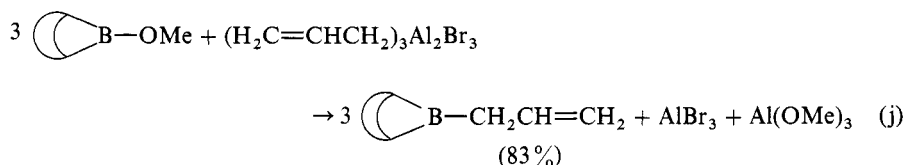
The reactions of dialkyl- or diarylborinic acid esters and alkylboronic acid esters with organolithium, Mg or Al compounds may serve to prepare unsymmetrical BR_2R' and BAR_2Ar' organoboranes^{16–21}. Synthesis of such organoboranes usually proceeds without complications:



In the aromatic series, treatment of the intermediate Li triarylalkoxyborate, with hydrochloric acid results in displacement of the aryl group even more easily than for Li diaryldialkoxymborates²². This difficulty can be overcome using amines instead of hydrochloric acid or starting with the amine complexes of diarylborinic acids²³:

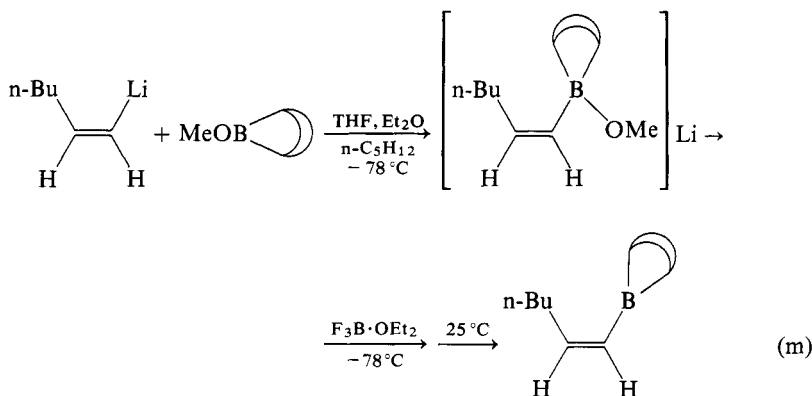


where py is pyridine. Dialkylallylic- and dialkylalkynylboranes are also obtained by these methods^{7,24,25}:

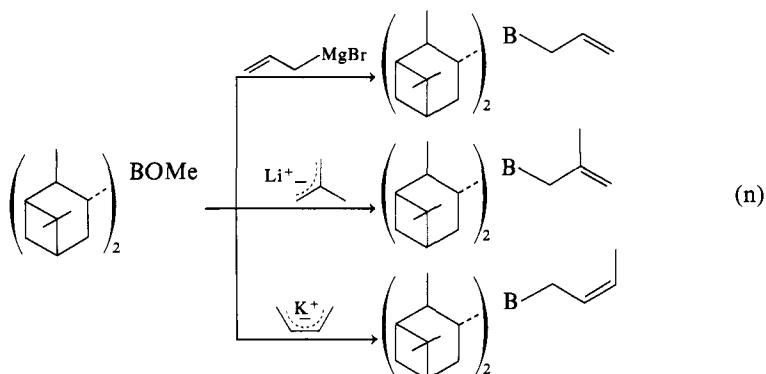


Allyllithium gives even higher yields of B-allyl-9-BBN than allylaluminum sesquibromide. However, the stoichiometry of the reaction must be controlled to avoid the formation of a diallyl ate complex, and the isolation of product is not simple. Alkylations of B-methoxy-9-BBN with the RMgX reagents meet with limited success. Only the methyl group is quantitatively transferred. Lower yields are obtained with other groups¹⁶, e.g., n-Bu (42%), Ph (27%).

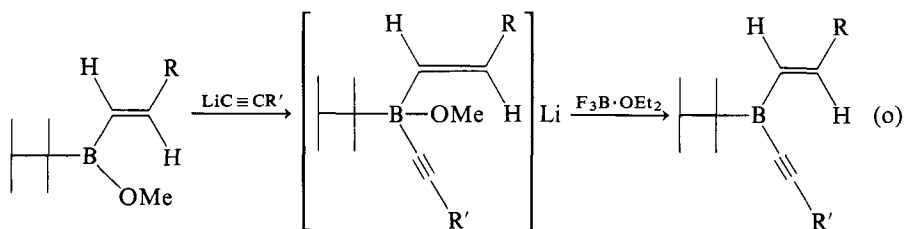
Synthesis of B-[Z]-1-alkenyl-9-borabicyclo[3.3.1]nonanes, not available by hydroboration, is achieved via vinylic organolithiums²⁶:



Synthetically important chiral dialkylallylicboranes are prepared from dialkylborinic esters and allylic derivatives of Li,²⁷ K²⁸ and Mg²⁷:



In the synthesis of alkylalkenylalkynylboranes, the third substituent is introduced similarly²⁹.



(H. C. BROWN, M. ZAIDLEWICZ)

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27. P. K. Jadhav, K. S. Bhat, P. T. Perumal, H. C. Brown, *J. Org. Chem.*, **51**, 432 (1986).
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29. H. C. Brown, D. Basavaiah, N. G. Bhat, *Organometallics*, **2**, 1468 (1983).

5.3.2.5. from Boron Hydrides

5.3.2.5.1. by Addition to Olefins and Acetylenes (Hydroboration).

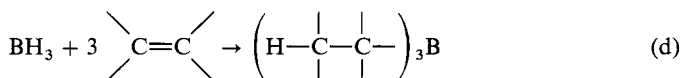
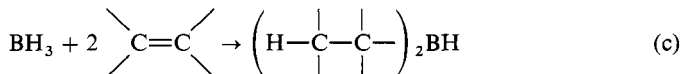
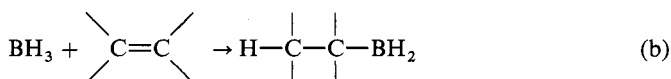
General Considerations. The addition of boron-hydrogen across a double or triple bond (hydroboration) is an important method for making organoboranes; it provides access to these compounds from available olefinic and acetylenic precursors. Organoboranes are versatile synthetic intermediates and selective reducing agents¹⁻²⁶. In this section, the role of the hydroboration reaction in B—C bond making is emphasized.

The first studies on the reaction of olefins and acetylenes with diborane met with little success. In the gas phase, olefins react sluggishly over long periods at elevated T to give mixtures^{27,28}. Acetylene gives polymeric organoboranes^{29,30}. However, in ether solvents, the addition is fast and quantitative at 0°C¹⁻³. The catalytic effect of ethers is attributed to the formation of weak, reactive borane complexes^{1-4,20,31}:



Other weak electron-pair donor bases, e.g., sulfides^{3,32}, also catalyze the addition, but the stronger complexes formed by amines require elevated T³³⁻³⁵.

Mono-, di- and trialkylboranes may be obtained from olefins and the trifunctional borane molecule¹⁻³:



Simple, unhindered alkenes react to the trialkylborane stage. With trisubstituted and some hindered disubstituted alkenes, the reaction may stop at the dialkylborane stage. Tetrasubstituted and some hindered di- and trisubstituted alkenes, e.g., 2,3-dimethyl-2-butene¹⁻³, (E)-2,2,5,5-tetramethyl-3-hexene³⁶ and 2,4,4-trimethyl-2-pentene³⁷ react rapidly only to the monoalkylborane stage. Rarely, when the tetrasubstituted double bond is incorporated in a cyclic structure, hydroboration under normal conditions fails³⁸⁻⁴⁰. However, such double bonds may react under more forcing conditions^{38,41-44}.

Several mono- and dialkylboranes obtained by controlled hydroboration of olefins are valuable hydroborating agents. Heterosubstituted borane derivatives are also available, and the search for new reagents, including higher boranes, continues^{32,45-47}. The most frequently used are shown in Fig. 1 where for convenience monomeric forms are presented.

5.3. The Formation of Bonds

35

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.5. from Boron Hydrides

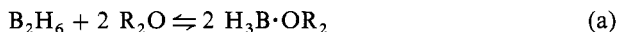
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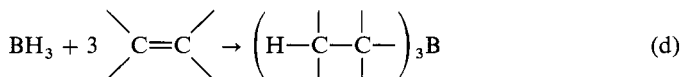
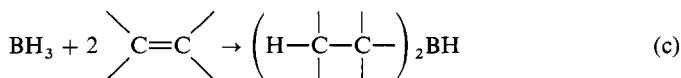
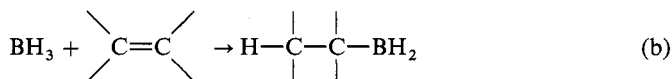
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Mono-, di- and trialkylboranes may be obtained from olefins and the trifunctional borane molecule¹⁻³:



Simple, unhindered alkenes react to the trialkylborane stage. With trisubstituted and some hindered disubstituted alkenes, the reaction may stop at the dialkylborane stage. Tetrasubstituted and some hindered di- and trisubstituted alkenes, e.g., 2,3-dimethyl-2-butene¹⁻³, (E)-2,2,5,5-tetramethyl-3-hexene³⁶ and 2,4,4-trimethyl-2-pentene³⁷ react rapidly only to the monoalkylborane stage. Rarely, when the tetrasubstituted double bond is incorporated in a cyclic structure, hydroboration under normal conditions fails³⁸⁻⁴⁰. However, such double bonds may react under more forcing conditions^{38,41-44}.

Several mono- and dialkylboranes obtained by controlled hydroboration of olefins are valuable hydroborating agents. Heterosubstituted borane derivatives are also available, and the search for new reagents, including higher boranes, continues^{32,45-47}. The most frequently used are shown in Fig. 1 where for convenience monomeric forms are presented.

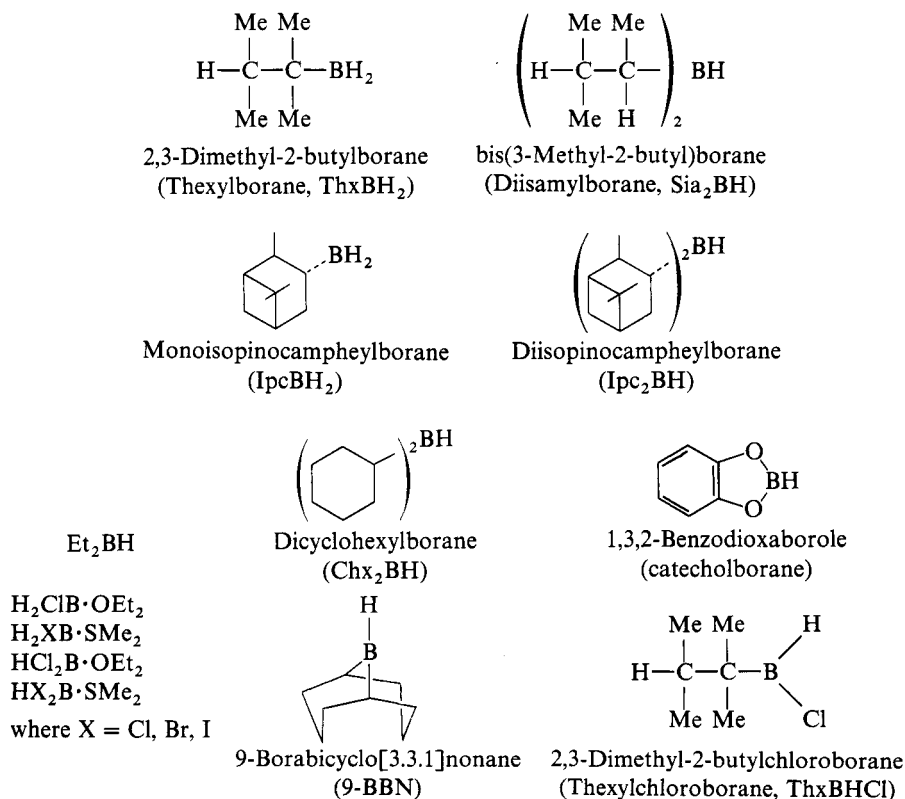


Figure 1.

With this spectrum of reagents, virtually all unsaturated hydrocarbons can be hydroborated. Moreover, many functional groups are tolerated in hydroboration with substituted borane derivatives, since double and triple C—C bonds react more rapidly than most other functionalities (see Table 1). Only aldehydes, ketones and carboxylic groups must be protected. Consequently, for the first time, functionalized organometallics are available. Chiral organoboranes of high optical purity can be prepared^{13,53–55}. This extends the scope of hydroboration. No isomerization of the organic moiety is observed under normal conditions. Although the addition is reversible, thermal dissociation of organoboranes occurs rarely at <100°C^{56–63}. However, at higher T, isomerization involving migration of the B—C bond may occur^{63–68}. The reaction is usually performed at 0°C or at RT. Most conveniently, a standardized solution of hydroborating agent is used, and the organoborane is isolated simply by removing the solvent. Alternatively, the hydroborating agent may be generated in situ³. Diborane can be prepared by several methods^{69–78}, but most often it is generated from Na[BH₄] with F₃B·OEt₂ and absorbed in tetrahydrofuran (THF) where it forms the H₃B·THF complex³.

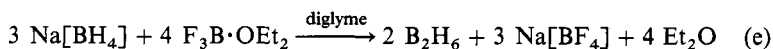
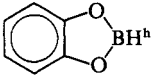


TABLE 1. REACTIVITIES OF REPRESENTATIVE FUNCTIONAL GROUPS TOWARD SELECTED BORANES^a

Functional groups/boranes	H ₃ B·THF ^b	ThxBH ₂ ^{c,d}	Sia ₂ BH ^{e,f}	9-BBN ^g	
Alkyne	f	f	f	f	m
Alkene	f	f	f	f	s
Aldehyde	f	f	f	f	f
Ketone	f	f	f	f	m
Carboxylic acid	f	vs	n	vs	m
Nitrile	f	vs	vs	vs	s
Lactone	f	s	f	m	—
Carboxylic acid anhydride	f	f	vs	vs	m
Epoxide	s	s	s	vs	m
Ester	s	vs	n	m	s
Amide	s	s	s	s	m
Acid chloride	n	n	n	f	s
Nitro	n	n	n	n	n
Alkyl halide	n	n	n	n	n

^a f, fast; m, moderate; s, slow; vs, very slow; n, no reaction.

^b Ref. 48.

^c ThxBH₂ = 2,3-dimethyl-2-butylborane.

^d Ref. 49.

^e Sia₂BH = bis(3-methyl-2-butyl)borane.

^f Ref. 50.

^g Ref. 51. 9-BBN = 9-borabicyclo[3.3.1]nonane.

^h Ref. 52.

Solutions of ca. 1 M are commercially available. However, choice of solvent is limited to THF, and borane solutions > ca. 2 M cannot be prepared. These inconveniences are avoided with the H₃B·SMe₂ complex^{3,79,80}, which can be obtained as a pure 1:1 adduct, ca. 10 M in BH₃, stable indefinitely at RT. The complex is soluble in ethers, dichloromethane, benzene, etc. Dimethyl sulfide does not interfere in the isolation of products since it does not complex strongly with organoboranes. Consequently, its low bp permits removal from the mixture by distillation. Another useful reagent, the borane 1,4-oxathiane complex, shows solubility characteristics similar to H₃B·SMe₂ and can be ≤ ca. 8 M in BH₃³². Because 1,4-oxathiane is moderately soluble in H₂O, it can be separated from the products by extraction into H₂O. The above-mentioned borane complexes show similar regioselectivity in the hydroboration of olefins. Terminal monosubstituted alkenes react with borane to place 94% of the boron at the terminal position. Disubstituted 1-alkenes and trisubstituted olefins undergo hydroboration to place 99% of the boron at the terminal position. Low selectivity is achieved in the hydroboration of disubstituted internal alkenes and acetylenes, even when the substituents differ in size, indicating low sensitivity of borane to steric effects. Organoboranes obtained from simple 1-alkenes contain 6% of boron placed at the internal position. Their purity is sufficient for many synthetic purposes. However, such product may contain up to 18% of di-n-alkyl-s-alkylborane in addition to tri-n-alkylborane. This may complicate further transformations involving migration of alkyl groups.

The above inconveniences are circumvented by the application of substituted borane derivatives, e.g., Si_2BH and 9-BBN (see Fig. 1 for definitions), which react with high regioselectivity and sensitivity to steric factors. Thus, 1-alkenes and 1-alkynes are hydroborated at the terminal position. The internal unsymmetrically disubstituted alkenes are also selectively hydroborated. The clean transformation of 1-alkynes into vinylboranes—not possible with borane—can be achieved with these reagents (Fig. 2).

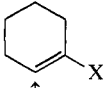
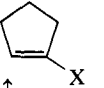
The regioselectivity in hydroboration of functionalized olefins and acetylenes with borane is influenced by substituents located in the vinylic and allylic positions. For 3-butenyl derivatives, 11–18% of the products have boron at the internal position⁸⁹. The effect fades with the increasing distance of the functional group from the double bond. In the addition to vinylic derivatives, the inductive and mesomeric effects play an important role. Thus, the substituents with a strong +M effect, e.g., $-\text{OR}$ ⁹⁰ and $-\text{NR}_2$ ^{91–93} direct boron to the β position, the effect being stronger for the $-\text{OR}$ group. The reverse is observed for $-M$ substituents, such as silicon^{94–96} and boron^{97–100}.

Chlorine and bromine with inductive electron withdrawal ($-I$) > mesomeric electron donation ($+M$) direct boron to the α position, the degree of selectivity varying with structure^{90,101–105}. The direction of addition to allylic derivatives is influenced by steric and inductive effects of the substituent¹⁰⁶. Electron-withdrawing groups direct the boron

	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CH}_2\text{C}(\text{H}_3)=\text{CH}_2$	$\text{PhCH}=\text{CH}_2$
	$\uparrow \quad \uparrow$	$\uparrow \quad \uparrow$	$\uparrow \quad \uparrow$
$\text{H}_3\text{B} \cdot \text{THF}$ ⁸¹	6 94	1 99	19 81
9-BBN ^{82,83}	0.1 99.9	0.2 99.8	2 98
Si_2BH ⁸⁴	1 99	—	2 98
$\text{H}_2\text{ClB} \cdot \text{OEt}_2$ ⁸⁵	0.5 99.5	0.1 99.9	4 96
$\text{ThxHClB} \cdot \text{SMe}_2$ ⁸⁶	0.6 99.4	trace >99.9	<1 >99
	$\text{CH}_3\text{H}_2\text{C} \quad \text{CH}_3$ $\diagdown \quad \diagup$ $\text{CH}=\text{CH}$ $\uparrow \quad \uparrow$	$(\text{CH}_3)_2\text{HC} \quad \text{CH}_3$ $\diagdown \quad \diagup$ $\text{CH}=\text{CH}$ $\uparrow \quad \uparrow$	
$\text{H}_3\text{B} \cdot \text{THF}$ ⁸¹	45 55	43 57	
9-BBN ^{82,83}	34 66	0.2 99.8	
Si_2BH ⁸⁴	—	3 97	
$\text{H}_2\text{ClB} \cdot \text{OEt}_2$ ⁸⁵	42 58	40 60	
$\text{ThxHClB} \cdot \text{SMe}_2$ ⁸⁶	24 76	3 97	
	H_3C $ $ $\text{CH}_3\text{C}=\text{CHCH}_3$ $\uparrow \quad \uparrow$	$(\text{CH}_3)_2\text{CHC} \equiv \text{CCH}_3$ $\uparrow \quad \uparrow$	
$\text{H}_3\text{B} \cdot \text{THF}$ ⁸¹	2 98	25 75	
9-BBN ^{82,83}	0.2 99.8	4 96 ⁸⁷	
Si_2BH ⁸⁴	—	7 93 ⁸⁸	
$\text{H}_2\text{ClB} \cdot \text{OEt}_2$ ⁸⁵	0.3 99.7	—	
$\text{ThxHClB} \cdot \text{SMe}_2$ ⁸⁶	0.4 99.6	—	

Figure 2.

TABLE 2. DIRECTIVE EFFECTS IN THE HYDROBORATION OF ALLYLIC AND VINYLIC DERIVATIVES WITH $\text{H}_3\text{B}\cdot\text{THF}$ AND 9-BBN

X	$\text{CH}_2=\text{CHCH}_2\text{X}$		$\text{CH}_3\text{CH}=\text{CHCH}_2\text{X}$		$\text{CH}_2=\text{CHX}$		
	BH_3^a	9-BBN ^b	BH_3^c	9-BBN ^b	BH_3	BH_3^d	$\text{BH}_3^{b,d}$ 9-BBN ^b
OH	82		10	0			
Cl	60	98.9	0	0		40	major 99.5
OEt	81	98.4 ⁱ	16	8.3	major ^g	100	100 100
OAc	65	97.6	5	0		60	major 97
COOEt	83 ^e			0			
SiMe_3	100 ^f	100 ^f			40 ^f	8 ^h	
Ts	55						

^a Ref. 107.

^b Ref. 104; 9-BBN = 9-borabicyclo[3.3.1]nonane.

^c Ref. 106.

^d Ref. 90.

^e Ref. 108.

^f Ref. 96.

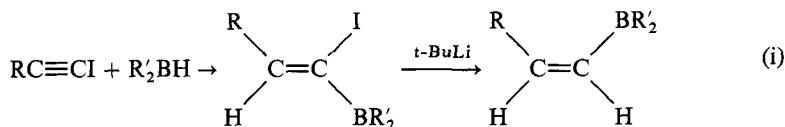
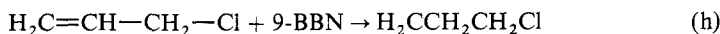
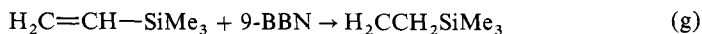
^g Ref. 109.

^h Ref. 62.

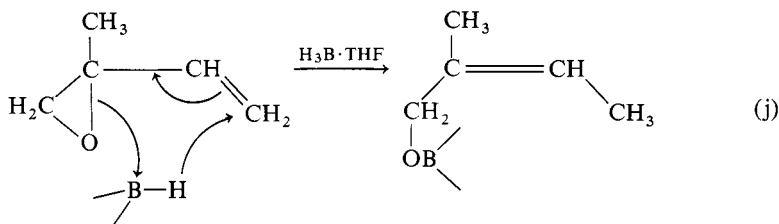
ⁱ X = OCH_3 .

atom to the β position, the effect increasing with the increasing electronegativity of the substituent. Directive effects in the hydroboration of functionalized acetylenes follow a similar pattern¹⁰. The electronic effects exerted by the substituents can be overcome by application of bulky, sterically demanding hydroborating agents (see Table 2).

The possibility of controlling the direction of addition is important because isomerically pure, substituted organoboranes can be prepared^{3,96,104,105}, e.g.:

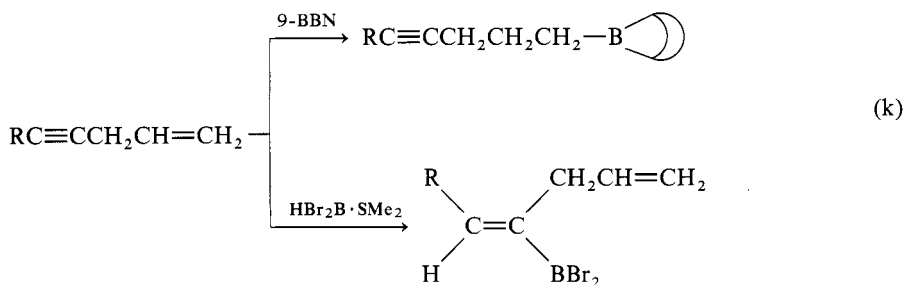


Regioselectivity of hydroboration of heterocycles bearing an endocyclic double bond with borane-dimethyl sulfide and dialkylboranes such as 9-BBN, Sia_2BH and dicyclohexylborane makes possible the synthesis of heterocyclic alcohols in good yields¹¹⁰. Directive effects in the hydroboration of vinyl heterocycles with the above-mentioned hydroborating agents are similar to those realized for styrene. However, vinylpyridines show differences depending on the isomer. Thus *o*- and *p*-vinylpyridines give β -organoboranes as the major products whereas the α -organoborane is formed predominantly from *m*-vinylpyridine¹¹¹. Finally, functional groups direct the addition, not only via steric and electronic effects but also by the formation of cyclic transition states when properly located^{112,113}:



The effects influencing regioselectivity in hydroboration are also responsible for reactivity differences exhibited by structurally different olefins toward hydroborating agents. Whereas B_2H_6 is insensitive to structural changes in alkenes, substituted boranes are more discriminating. The relative reactivities of olefins toward Sia_2BH , 9-BBN, catecholborane, $\text{Br}_2\text{HB}\cdot\text{SMe}_2$, and ThxBHCl (Thx = *tert*-hexyl, 2,3-dimethyl-2-butyl; see Fig. 1 for other definitions) are presented in Table 3.

Thus the reagents differ in their sensitivity to steric and electronic effects. Their reactivities vary over the range 10^4 – 10^5 . Hydroboration with Sia_2BH is controlled predominantly by steric effects; e.g., 2-methyl-1-pentene is less reactive toward Sia_2BH than 1-hexene, whereas the reverse is observed for 9-BBN, demonstrating its greater sensitivity to electronic effects. The reactivity of 9-BBN toward 1-alkenes allows selective hydroboration of terminal double bonds in the presence of internal unsaturation. *tert*-Hexylchloroborane shows large differences in the reactivities of *cis*/*trans*-olefin pairs, the *cis* isomer being more reactive. Dibromoborane is exceptionally reactive toward acetylenes. These differences can be utilized in selective hydroborations, e.g.:



The reactivity and regioselectivity in hydroboration is controlled by polarization of the B—H bond and by a combination of electronic and steric substituent effects in the unsaturated system. The favored orientation is shown in Fig. 3.

TABLE 3. RELATIVE REACTIVITIES OF REPRESENTATIVE OLEFINS TOWARD Si_2BH , 9-BBN, $\text{ThxHClB}\cdot\text{SMc}_2$, CATECHOLBORANE AND $\text{Br}_2\text{HB}\cdot\text{SMc}_2$ (1-Hexene = 100)

Olefin	Relative reactivity					
	$\text{Si}_2\text{BH}^{\text{a,b}}$	9-BBN ^b	$\text{ThxHCl}\cdot\text{SMc}_2^{\text{e}}$	Catecholborane ^d	$\text{Br}_2\text{BH}\cdot\text{SMc}_2^{\text{e}}$	
1-Hexene	100	100	100	100	100	
1-Octene	108	110	98	96	95.2	
Cyclooctene	26	6.9	89	12.2	312	
2-Methyl-1-pentene	4.9	194	41	53	2050	
Cycloheptene	7	7.6	12	20.9	66	
(Z)-3-Hexene	2	0.68 ^f	11	33.8	42.1	
(Z)-2-Pentene	2	1	8.5	—	—	
(Z)-4-Methyl-2-pentene	0.5	0.53 ^f	7.7	6.1	40.2	
Cyclopentene	1.4	7.2	2.2	6.3	16.5	
Styrene	—	2.5	1.1	26.7	2.67	
(Z)-4,4-Dimethyl-2-pentene	0.08	0.38	0.28	—	—	
(E)-3-Hexene	0.2	0.32 ^f	0.12	9.3	22.6	
α -Methylstyrene	2.3	14	0.11	10.3	—	
(E)-4-Methyl-2-pentene	0.1	0.16 ^f	0.07	3.4	12	
Cyclohexene	0.01	0.067	0.072	4.1	1.00	

^a In THF at 0°C; Ref. 114.

^b In THF at 25°C; Ref. 115.

^c In CH_2Cl_2 at 25°C; Ref. 116.

^d Ref. 117.

^e Ref. 118.

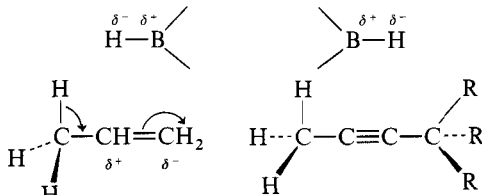
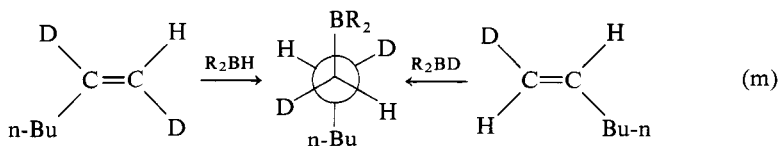
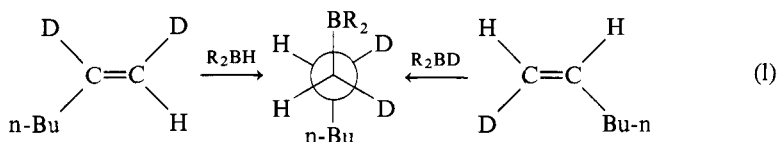
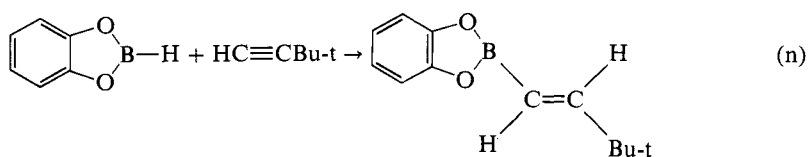


Figure 3.

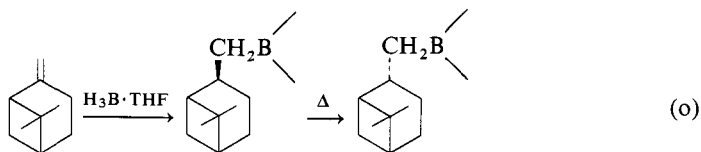
The addition is exclusively *cis*¹⁻³, as demonstrated in hydroboration-oxidation reactions, assuming retention of configuration in the oxidation step. *Cis* addition of the B—H bond is demonstrated in the NMR study of organoboranes derived from deuterated 1-hexene and dialkylboranes^{120,121}:



The hydroboration of acetylenes also involves *cis* addition, leading to stereodefined vinylic organoboranes^{3,122,123}:

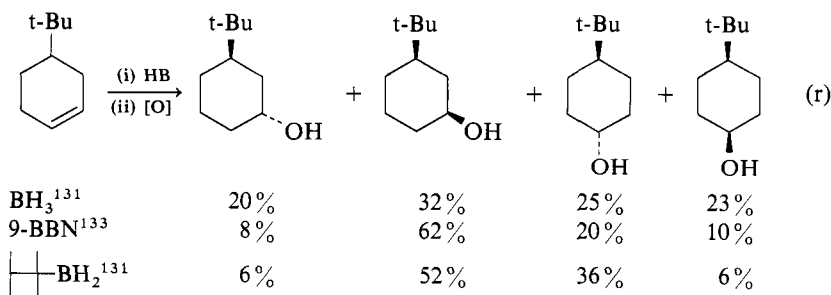
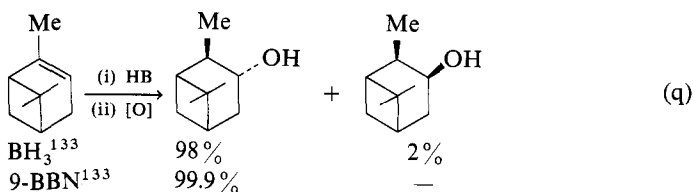
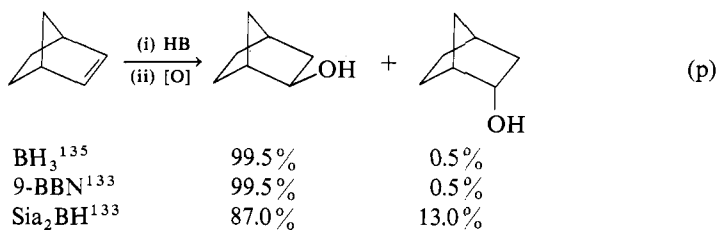


Olefins are approached by the hydroborating agent from the less hindered face of the double bond. Thermodynamically less stable organoboranes are often formed, as demonstrated for β -pinene^{124,125} and camphene¹²⁶:



The stereoselectivity of addition is high, with olefins having one face of the double bond more hindered than the other. Where this difference is small, low selectivity

results^{127–132}. This difficulty is often circumvented by application of bulky, sterically demanding hydroborating agents. Among all boranes, 9-BBN seems to be most sensitive to subtle steric differences¹³³. Other advantages of 9-BBN are its reactivity and the thermal stability of B-alkyl-9-BBN derivatives¹³⁴ (cf. ref. 63). Consequently, the hydroboration of systems showing low reactivity, e.g., trisubstituted olefins, can be carried out at moderate T without danger of thermal isomerization^{133,134}. Representative examples of stereoselectivity in hydroboration are:



Thus steric approach controls the reaction, and hydroboration proceeds by *cis* addition from the less hindered face of the double bond^{1–3} to add the boron to the less substituted carbon atom.

Functional groups present may influence the stereochemistry of addition. Thus, in the hydroboration of 3-hydroxy-, 3-methoxy- or 3-chlorocyclohexene¹³⁶ and conjugated cyclohexenones^{137–140}, the double bond is attacked predominantly from the direction opposite to the substituent owing to steric interactions of the approaching borane with the functional group:

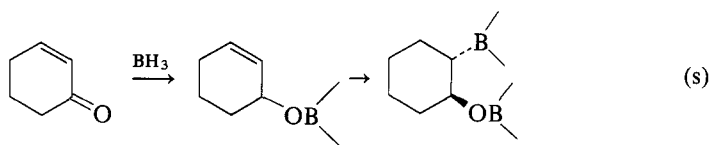
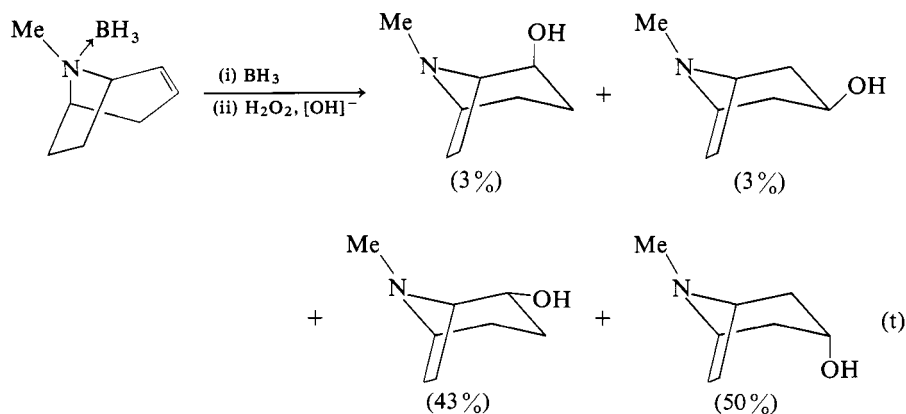




Figure 4.

Amine groups, by strong complexation of borane, may render one face of the double bond more hindered and direct the attack to the opposite face^{141,142}:



However, groups complexing borane weakly may facilitate its attack from the same side^{143–145} (see Fig. 4).

The characteristic features of hydroboration, originally accounted for in terms of the four-center transition state with partial charges on the participating atoms^{1,3,81} (see Fig. 5). This simple model, based on qualitative observations, is a useful working hypothesis. However, hydroboration proceeds best in solution where ethereal solvents or other electron-pair donor bases play an important role, and must be taken into account in mechanistic considerations. An *ab initio* calculation on the reaction of ethylene with $\text{H}_3\text{B}\cdot\text{OH}_2$ suggests an $\text{S}_{\text{N}}2$ -type direct displacement of H_2O by the alkene¹⁴⁶. However, the experimental results disagree. Although kinetic studies on the reaction of diborane with unhindered olefins in ethers are hampered by the complexity of various equilibria¹⁴⁷, involving monomer-solvent, monomer-dimer and redistribution, certain hindered olefins can be hydroborated in a simple reaction to the monoalkylborane stage. For such reactions, kinetic analysis is possible. The results obtained for $\text{H}_3\text{B}\cdot\text{SMe}_2$

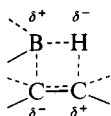
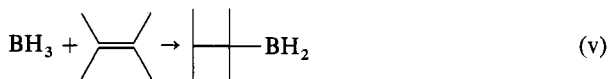
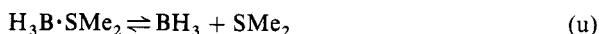


Figure 5.

complex with 2,3-dimethyl-2-butene in toluene reveal a two-step dissociation mechanism. The complex first liberates BH_3 in an equilibrium, and then the free BH_3 reacts with the alkene¹⁴⁸:



Borane-amine complexes react similarly^{148,149}. Kinetics of hydroboration of representative alkenes with well-characterized dialkylborane dimers show that the dimer initially dissociates into the monomer in an equilibrium:



The monomer subsequently reacts with the alkene^{150–155}:



Similarly, the reaction of 9-BBN-electron-pair donor base complexes¹⁵⁵ and $\text{Br}_2\text{HB} \cdot \text{SMe}_2$ ¹⁵⁶ with alkenes follows such a dissociation pathway:



where L = an electron-pair base. These results establish dissociation as general for the hydroboration of alkenes in solution utilizing either borane-electron-pair donor base complexes or dialkylborane dimers^{148,157}. It also accounts for the kinetics of 2,3-dimethyl-2-butene with $\text{H}_3\text{B} \cdot \text{THF}$ in THF⁵¹. The addition of free borane to a double bond is a concerted process. In the gas phase, a loose π complex is formed early along the reaction coordinate¹⁵⁸. Calculations on the reaction of BH_3 with ethylene predict a two-step process involving π -complex formation, but the energy profile remains uncertain^{159–166}. In the concerted addition, the participation of the p orbital on boron removes symmetry restrictions for 2π 's + 2δ 's addition. Donation of electrons from the π orbital of an olefin to the p orbital on boron and a back donation from the B—H bond to the π^* orbital would account for a concerted reaction. The transition state for such a process is shown in Fig. 6.

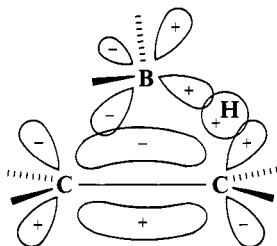
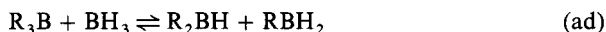


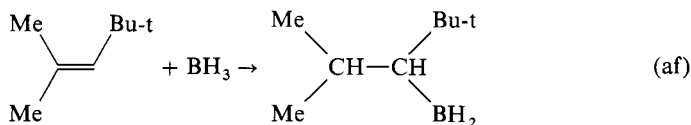
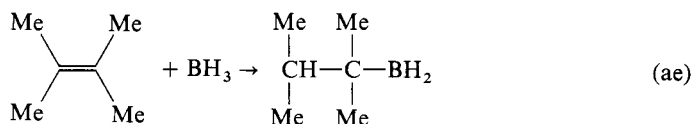
Figure 6.

Models accounting for hydroboration stereoselectivity have been advanced.^{167–170.}

(ii) **Organoboranes with One B—C Bond.** Hydroboration of olefins with 1:1 $\text{H}_3\text{B}\cdot\text{THF}$ or $\text{H}_3\text{B}\cdot\text{SMe}_2$ proceeds rapidly beyond the monoalkylborane stage. In the presence of unreacted borane, an equilibrium is reached owing to redistribution:

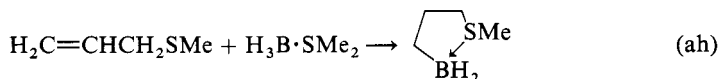
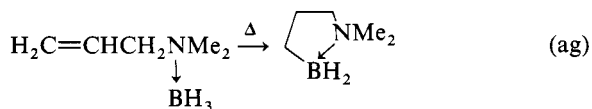


Hindered olefins react fast to the monoalkylborane stage, further reaction being slow. By control of the reaction conditions, monoalkylboranes, e.g., *thexylborane*³ and 2,4,4-trimethyl-3-pentylborane¹⁷¹, can be obtained in this way:

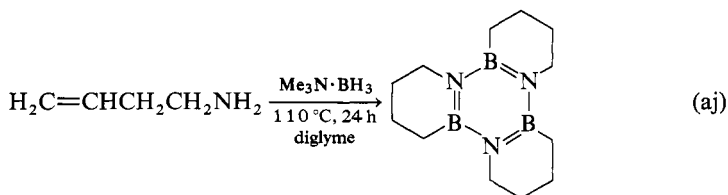
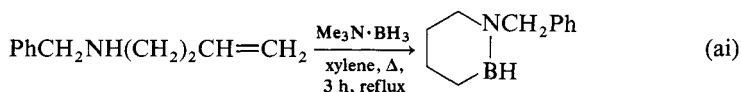


For moderately hindered olefins, the redistribution equilibria may be favorable to the monoalkylborane, e.g., for α -pinene¹⁷². The equilibrium is reached after 120 h at 25°C and the mixture is composed of monoisopinocampheylborane (IpcBH_2 , 91%), BH_3 (4.5%) and diisopinocampheylborane (Ipc_2BH , 4.5%). The small amount of BH_3 can be removed by pumping off the solvent and addition of pentane, followed by an equivalent amount of tetramethylethylenediamine (TMED). The $\text{TMED}\cdot\text{BH}_3$ complex precipitates and can be filtered. By further addition of the amine, the $\text{TMED}\cdot 2 \text{IpcBH}_2$ complex is formed as a white solid.

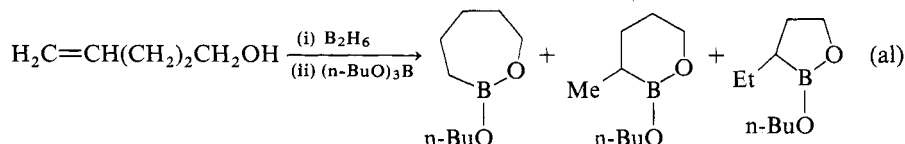
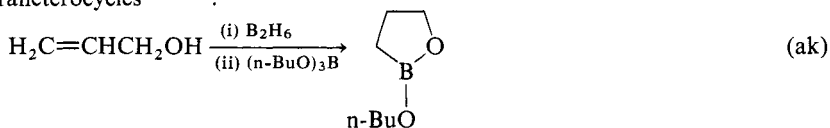
Hydroboration of certain functionalized alkenes with borane also stops at the monoalkylborane stage. Thus, in the reaction of borane with unsaturated amines and sulfides, the initial addition product may undergo intramolecular complexation to form a cyclic product^{173,174}:



These complexes are not hydroborating agents. Upon heating, the monoalkylboranes derived from primary and secondary amines are transformed into azaboraheterocycles^{175,176}:



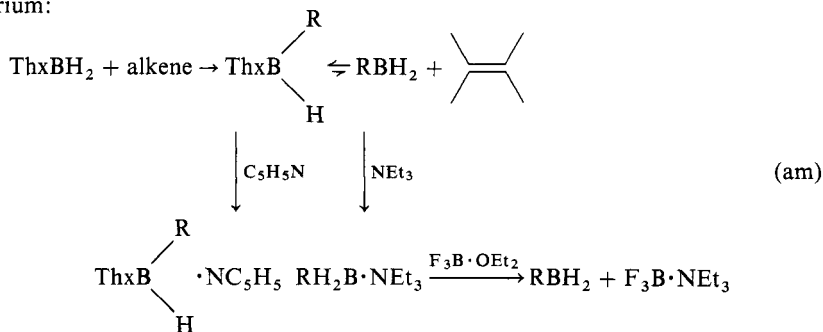
Similarly, hydroboration of unsaturated aliphatic alcohols, followed by treatment with trialkoxyboranes or by thermal isomerization, leads to the corresponding oxaboraheterocycles^{177,178}:



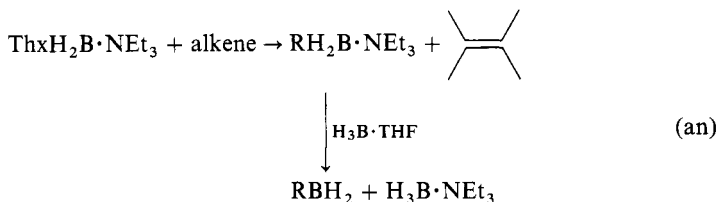
Five-, six- and seven-membered rings are favored in the thermal isomerization [see Eqs. (ai)–(al)].

Other unsaturated nitrogen, oxygen and sulfur derivatives of alkenes are also transformed into monoalkylborane derivatives^{5,11}.

An alternative approach to monoalkylboranes via hydroboration is based on thexylborane. The 1:1 reaction of di- and more reactive trisubstituted olefins, e.g., 1-methylcyclopentene at -20° to -25°C stops at the thexylmonoalkylborane stage¹⁷⁹. Less reactive trisubstituted olefins, e.g., 1-methylcyclohexene and α -pinene, react slowly, and the corresponding thexylmonoalkylboranes are formed only in 80% and 75% yields, respectively. At 0°C , dehydroboration of 2,3-dimethyl-2-butene occurs owing to the equilibrium:

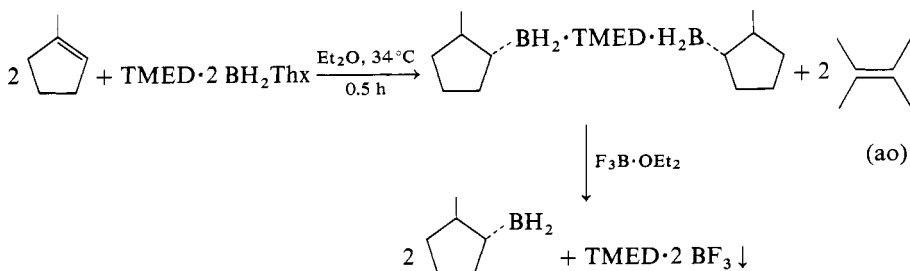


The $\text{RH}_2\text{B}\cdot\text{NEt}_3$ adducts can also be obtained by hydroboration of olefins with $\text{ThxH}_2\text{B}\cdot\text{NEt}_3$ complex^{180,181}. Treatment with $\text{F}_3\text{B}\cdot\text{OEt}_2$ or $\text{H}_3\text{B}\cdot\text{THF}$ liberates free monoalkylborane.



Alcoholysis gives the corresponding alkyl boronates (see Table 4).

The procedure suffers, however, from high solubility of $\text{H}_3\text{B}\cdot\text{NEt}_3$ and $\text{F}_3\text{B}\cdot\text{NEt}_3$ in THF and the liquid nature of $\text{RH}_2\text{B}\cdot\text{NEt}_3$ complexes, rendering product isolation difficult. These problems are avoided by using TMED instead of NEt_3 . The $\text{TMED}\cdot 2\text{BH}_2\text{Thx}$ bis adduct is prepared¹⁸² from thexylborane and TMED. The reagent hydroborates olefins, producing the corresponding $\text{TMED}\cdot 2\text{BH}_2\text{R}$ bis adducts in excellent yields¹⁷¹ (see Table 4). These air-stable, crystalline compounds can be stored neat or in THF solution for several weeks at RT without change. Treatment with $\text{F}_3\text{B}\cdot\text{OEt}_2$ liberates the free monoalkylborane. The $\text{TMED}\cdot 2\text{BF}_3$ adduct is insoluble in THF, Et_2O or pentane and precipitates quantitatively:

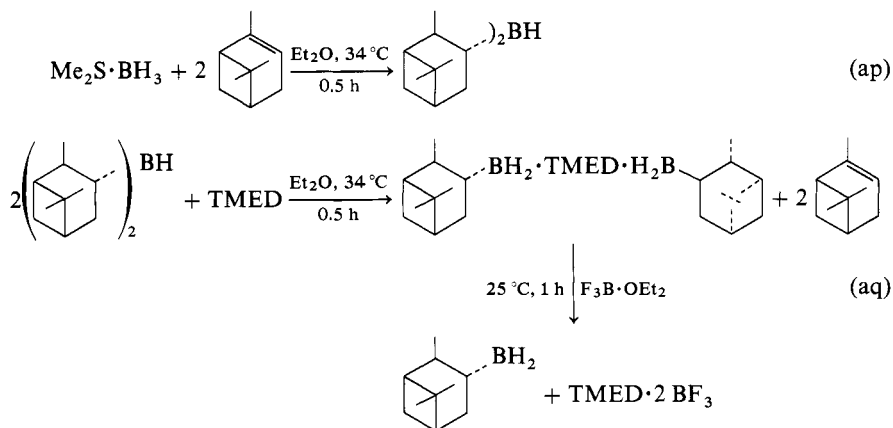


A limitation of the thexylborane route to monoalkylboranes is that it fails with monosubstituted 1-alkenes¹⁷⁹.

TABLE 4. SYNTHESIS OF DIMETHYLALKANEBORONATES VIA $\text{RH}_2\text{B}\cdot\text{NEt}_3$ AND $\text{TMED}\cdot 2\text{RBH}_2$ ADDUCTS^{171,179}

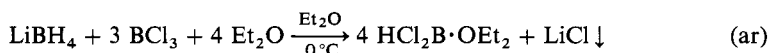
Alkene	$\text{Et}_3\text{N}\cdot\text{BH}_2\text{R}$	$\text{TMED}\cdot 2\text{BRH}_2$	
	Isolated yield (%)	Isolated yield (%)	mp ($^\circ\text{C}$)
(E)-3-Hexene	75	90	27-29
2-Methyl-1-pentene	70	—	—
Cyclopentene	—	96	105-106
Cyclohexene	77	98	100-101
2-Methyl-2-butene	—	84	90-92
1-Methylcyclopentene	80	98	123-124
α -Pinene	—	95	140-141
Norbornene	—	97	118-119

Thexylmonoalkylboranes are not unique in their behavior toward TMED. Dialkylboranes derived from moderately hindered olefins may also undergo dehydroboration by the action of TMED; e.g., Ipc_2BH is transformed into the $\text{TMED} \cdot 2 \text{BH}_2\text{Ipc}$ bis adduct and the reaction provides another convenient access to this chiralhydroborating agent¹⁸³:

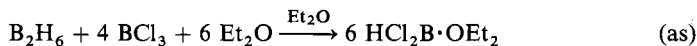


Thus, from optically impure α -pinene (94% e.e.), the TMED \cdot 2 BH₂Ipc bis adduct is obtained^{183,184} in optical purity approaching 100%. Other chiral monoalkylboranes¹⁸⁵ and boronic acids^{185–188} important in asymmetric synthesis^{53–55}, are available via IpcBH₂ and (Ipc)₂BH.

Organoboranes possessing one B—C bond in the molecule can also be obtained by hydroborating alkenes and alkynes with heterosubstituted borane derivatives, especially dihalogenoboranes, which can be stabilized by complexation with amines, phosphines, ethers and sulfides. The last two are useful complexing agents for both the preparation and the reactions of dihalogenoboranes^{3,189–192}. The most convenient synthesis^{3,191} of dichloroborane etherate is the reaction of LiBH_4 with BCl_3 in Et_2O :

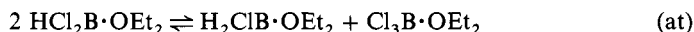


Lithium chloride precipitates and can be separated by decantation. Alternatively, $\text{HCl} \cdot \text{B} \cdot \text{OEt}_2$ is obtained^{193,194} from diborane with BCl_3 :



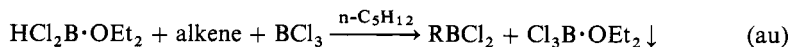
Dichloroborane coordinates strongly with ether, and neat $\text{HCl}_2\text{B}\cdot\text{OEt}_2$ can be obtained by concentrating its solution in Et_2O . It is a colorless liquid, mp -25 to -30°C , miscible with benzene, CCl_4 and THF, but not with paraffins. The reagent has only limited stability, cleaving ether even with storage at 0°C .³

Hydroboration of olefins with neat $\text{HCl}_2\text{B} \cdot \text{OEt}_2$ or in ethereal solutions is slow and accompanied by disproportionation leading to dialkylchloroboranes¹⁹¹:



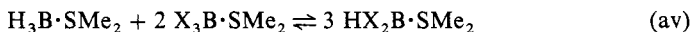
In contrast to $\text{HCl}_2\text{B}\cdot\text{OEt}_2$, $\text{H}_2\text{ClB}\cdot\text{OEt}_2$ hydroborates olefins rapidly and even a low concentration of this compound in the equilibrium mixture is sufficient to change the

reaction course. Low reactivity of dichloroborane in THF and Et₂O ether is the result of strong coordination with the solvent. In pentane, HCl₂B·OEt₂ also reacts sluggishly; however, addition of equimolar amounts of a stronger electron-pair acceptor acid, e.g., BCl₃, generates free dichloroborane, which reacts rapidly with olefins to give alkylidichloroboranes in excellent yield (see Table 5):



The products are transformed into the corresponding alkylboronic acids and their esters by hydrolysis or alcoholysis.

More general access to alkylidihalogenoboranes is by hydroboration of alkenes with dihalogenoborane–dimethyl sulfide complexes¹⁹⁶. The reagents (except difluoroborane) are synthesized by equilibration of H₃B·SMe₂ and trihalogenoborane–dimethyl sulfide complexes^{198,199}:



where X = Cl, Br, I. Neat HCl₂B·SMe₂ and HI₂B·SMe₂ are liquids at 25°C, whereas HBr₂B·SMe₂ is a solid (mp ≈ 30°–35°C). These complexes are stable indefinitely under N₂ at 25°C. Hydroboration of olefins with HCl₂B·SMe₂ is carried out in the same way as with HCl₂B·OEt₂ and requires addition of BCl₃ to generate free dichloroborane; but HBr₂B·SMe₂ and HI₂B·SMe₂ react directly with olefins in CH₂Cl₂ to give alkylidibromoboranes and alkylidiodoboranes, respectively (see Table 5). The products are strongly complexed with Me₂S and are isolated by distillation as RBr₂B·SMe₂ and RI₂B·SMe₂

TABLE 5. SYNTHESIS OF ALKYL- AND ALKENYLBORON DERIVATIVES BY HYDROBORATION OF ALKENES AND ALKYNES WITH HALOGENOBORANES

Alkyl- or alkenylboron derivative	Reagent	Yield (%)
Di-n-hexylchloroborane ^a	H ₂ ClB·OEt ₂	84
Methyl di-exo-norbornylborinate ^a	H ₂ ClB·OEt ₂	83
Di-n-butylchloroborane ^b	H ₂ ClB·SMe ₂	85
Di-i-butylchloroborane ^b	H ₂ ClB·SMe ₂	84
Di-n-butylbromoborane ^b	H ₂ BrB·SMe ₂	85
Di-s-butylbromoborane ^b	H ₂ BrB·SMe ₂	84
Di-n-hexyliodoborane ^b	H ₂ IB·SMe ₂	85
Dicyclopentylidoborane ^b	H ₂ IB·SMe ₂	86
n-Hexyldichloroborane ^d	HCl ₂ B·OEt ₂ , BCl ₃	81
3-Hexyldichloroborane ^c	HCl ₂ B·OEt ₂ , BCl ₃	77
n-Octyldichloroborane ^d	HCl ₂ B·SMe ₂ , BCl ₃	85
3-Hexyldibromoborane-dimethyl sulfide ^d	HBr ₂ B·SMe ₂	90
n-Octyldichloroborane-dimethyl sulfide ^d	HCl ₂ B·SMe ₂	69
(1E)-l-Hexen-1-yldibromoborane-dimethyl sulfide ^c	HBr ₂ B·SMe ₂	80
(3Z)-3-Hexen-3-yldibromoborane-dimethyl sulfide ^c	HBr ₂ B·SMe ₂	81
(1E)-5-Chloro-1-penten-1-yldibromoborane-dimethyl sulfide ^c	HBr ₂ B·SMe ₂	29

^a Ref. 85.

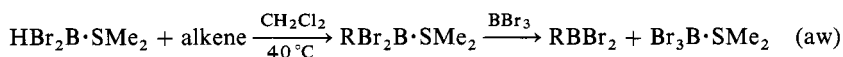
^b Ref. 195.

^c Ref. 191.

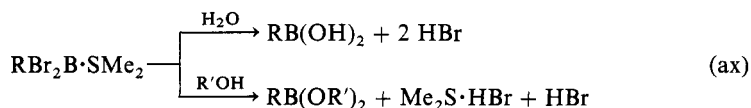
^d Ref. 196.

^e Ref. 197.

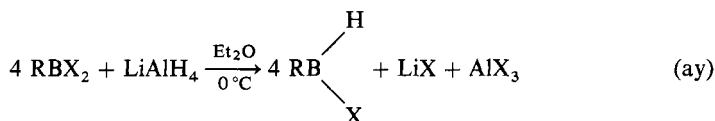
adducts. If free RBr_2B or RI_2B are required, they may be obtained by addition of BBr_3 or BI_3 , respectively¹⁹⁶:



Directive effects in the hydroboration of olefins with dihalogenoboranes are shown in Table 6. The addition is highly selective. Alkyldihalogenoboranes can be transformed into the corresponding alkylboronic acids or esters²⁰⁰:

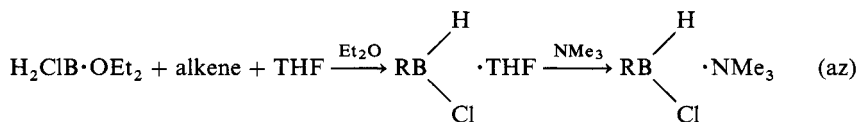


where $\text{R} = n\text{-C}_6\text{H}_{13}$, 3-hexyl, cyclopentyl, [1E]-1-heptenyl, [1E]-3,3-dimethyl-1-butenyl (hydrolysis), $n\text{-C}_6\text{H}_{13}$, [1E]-1-octenyl, cis-4-octenyl and $\text{R}' = \text{Me}$, $\text{HO}(\text{CH}_2)_2\text{-}$ (alcoholysis). Reduction of alkyldihalogenoboranes gives alkylmonohalogenoboranes, which are useful intermediates in the synthesis of di- and trialkylboranes with different alkyl groups²⁰²:

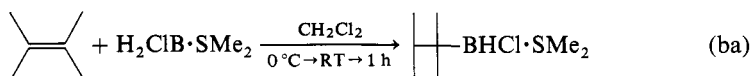


where $\text{X} = \text{Cl}, \text{Br}$.

Alkylmonochloroboranes can also be prepared by controlled hydroboration of olefins with ClBH_2 in ethers. With Et_2O , addition of equimolar THF prevents undesirable dihydroboration. Alkylmonochloroboranes disproportionate readily, and they must be complexed⁸⁵ for isolation:



In the monohydroboration of 2,3-dimethyl-2-butene with $\text{H}_2\text{BCl} \cdot \text{SMe}_2$, the formation of $\text{ThxHClB} \cdot \text{SMe}_2$ is quantitative in CH_2Cl_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$ or Et_2O , or without a solvent, despite the reagent's being an equilibrium mixture containing ca. 15% each of $\text{HCl}_2\text{B} \cdot \text{SMe}_2$ and $\text{H}_3\text{B} \cdot \text{SMe}_2$:



Solutions of $\text{ThxHClB} \cdot \text{SMe}_2$ in CH_2Cl_2 or Et_2O are stable for prolonged periods (2 months) at RT ⁸⁶.

Transformation of olefins into alkylboronic acid esters can be achieved also by 1,3,2-dioxabenzoborole. The reagent belongs to a group of oxa- and thioborolanes and borinanes^{52,78,123,203-205} (see Fig. 7). These compounds react slower than $\text{H}_3\text{B} \cdot \text{THF}$ or

TABLE 6. DIRECTIVE EFFECTS IN THE HYDROBORATION OF ALKENES WITH HALOGENOBORANES

Olefin	Isomeric alcohols	Relative yield of products							
		H_2CIB^a $\cdot\text{SMe}_2$	H_2BrB^a $\cdot\text{SMe}_2$	H_2IB^a $\cdot\text{SMe}_2$	H_2CIB^b $\cdot\text{OEt}_2$	HCl_2B^c $\cdot\text{SMe}_2$	HBr_2B^c $\cdot\text{SMe}_2$	HI_2B^c $\cdot\text{SMe}_2$	$\text{H}_3\text{B}^{b,d}$ $\cdot\text{THF}$
1-Hexene	1-hexanol	99.2	99.6	>99.5	>99.5	99	99.6	98	94
	2-hexanol	0.8	0.4	<0.5	<0.5	1	0.4	2	6
Styrene	2-phenylethanol	93	96	96	96	98	99	97	81
	1-phenylethanol	7	4	4	4	2	1	3	19
2-Methyl-1-pentene	2-methyl-1-pentanol	—	98	—	—	99.5	99	97	—
	2-methyl-2-pentanol	—	2	—	—	0.5	1	3	—
2-Methyl-2-butene	3-methyl-2-butanol	99.5	97	—	99.7	99.2	99	97	98
	2-methyl-2-butanol	0.5	3	—	0.3	0.8	1	3	2
1-Methylcyclopentene	trans-2-methylcyclopentanol	99.5	97.5	99.7	99.8	99.6	99.7	99.8	98.5
	1-methylcyclopentanol	0.5	2.5	0.3	0.2	0.4	0.3	0.2	1.5
	cis-2-methylcyclopentanol	0	0	0	0	—	—	—	0

^a Ref. 195.^b Ref. 85.^c Ref. 201.^d Ref. 81.

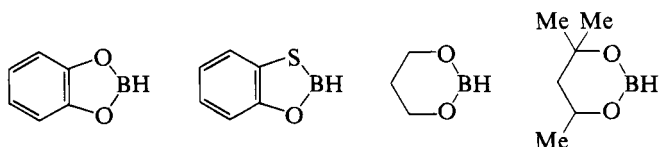
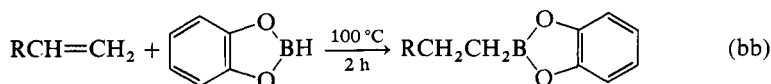


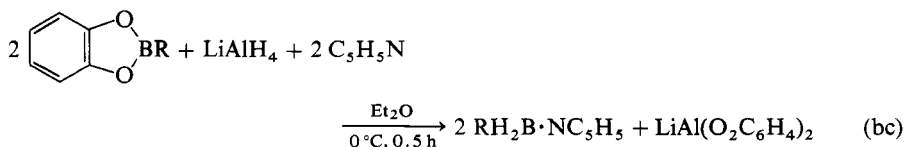
Figure 7.

dialkylboranes owing to donation of electrons from oxygen to the empty p orbital of boron, e.g., the hydroboration of 1-octene with 4,4,6-trimethyl-1,3,2-dioxaborinane proceeds at 100°C for 3 days in 28% yield¹²³. Other monocyclic compounds undergo disproportionation and must be stabilized by complexation. 1,3,2-Benzodioxaborole is free from these inconveniences. The aromatic ring decreases the back-donation of electrons from oxygen to boron, enhancing the reactivity. Consequently, olefins are hydroborated at 100°C in short periods to give the corresponding 2-alkyl-1,3,2-benzodioxaboroles in high yield^{52,122}:

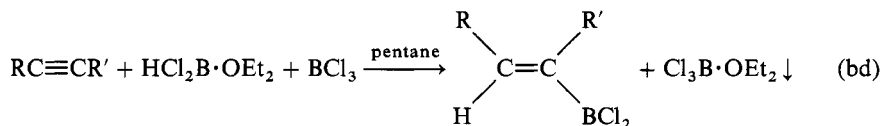


With Rh catalysts, hydroboration with this reagent proceeds even at RT²⁰⁶. Selective addition to a double bond in the presence of a keto group, not possible without a catalyst²⁰⁷, can be achieved²⁰⁶.

Greater regioselectivity is realized over $\text{H}_3\text{B} \cdot \text{THF}$. 2-Alkyl-1,3,2-benzodioxaboroles undergo rapid hydrolysis to the corresponding alkylboronic acids. Their reduction provides monoalkylboranes²⁰⁸:



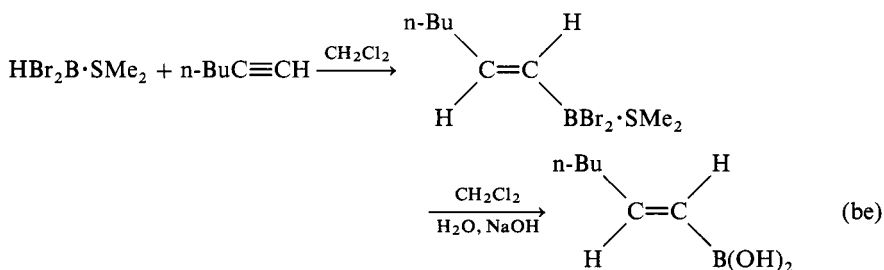
The attachment of one alkenyl group to boron can be achieved by the hydroboration of alkynes with dihalogenoboranes or 1,3,2-benzodioxaborole. Dichloroborane reacts sluggishly with alkynes in Et_2O or THF and the reaction is accompanied by disproportionation. However, in pentane the addition of BCl_3 generates the nascent HBCl_2 and the reaction proceeds to completion in 1 h at RT. Alkenyldichloroboranes are isolated by distillation in high yields¹⁹¹:



where $\text{R}' = \text{H}$ or R. Excess alkyne prevents undesirable dihydroboration.

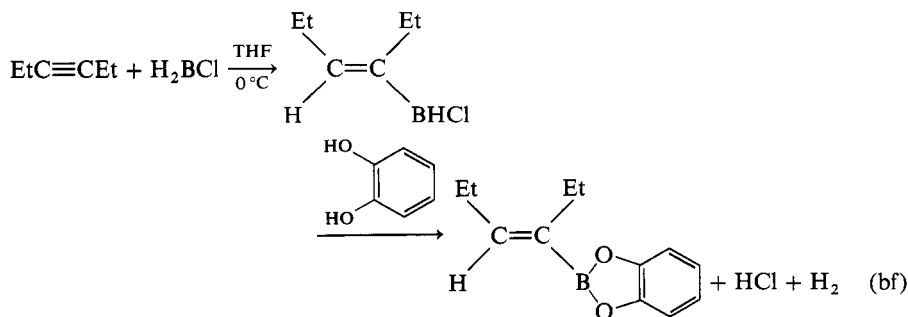
The more reactive $\text{HBr}_2\text{B} \cdot \text{SMe}_2$ hydroborates alkynes directly. The reaction stops at the monohydroboration stage without the need of xs alkyne to give the corresponding

alkenyldibromoborane-dimethyl sulfide complexes¹⁹⁷ (see Table 5). Hydrolysis with 2 equiv aq NaOH provides alkenylboronic acids:



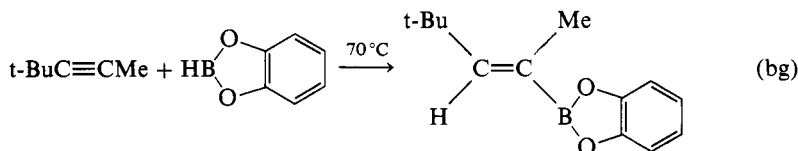
Dibromoborane-dimethyl sulfide exhibits high reactivity toward internal alkynes¹⁹⁷. The relative reactivity of 1-octene, 1-hexyne, (Z)-3-hexene and 3-hexyne is 100, 290, 20 and 5900, respectively. This makes possible selective hydroboration of internal alkynes in the presence of terminal unsaturation. With 1-bromoalkynes $\text{Br}_2\text{HB} \cdot \text{SMe}_2$ provides [Z]-1-dibromoalkenylboranes which can be transformed into [E]- or [Z]-1-alkenylboronic esters²⁰⁹.

The monohydroboration of alkynes can be achieved⁸⁵ also with H_2BCl . In THF, the reaction proceeds stepwise and can be controlled to stop at the alkenylchloroborane stage. The products are not isolated, but their formation is proved by transformation into the corresponding 2-alkenyl-1,3,2-benzodioxaboroles:



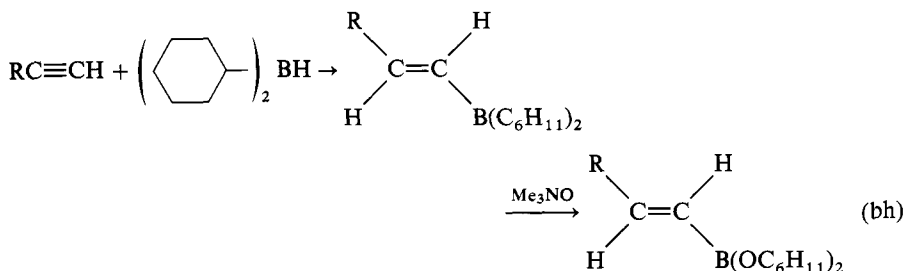
Yields of the catechol derivative of 3-hexyne and 1-hexyne are 84 and 44%, respectively, indicating substantial dihydroboration of the terminal triple bond. Quantitative yields of 2-alkenyl-1,3,2-benzodioxaboroles are obtained by hydroboration of alkynes with 1,3,2-benzodioxaborole^{122,210,211}.

The addition is highly regioselective and is exclusively cis; e.g., in the hydroboration of 4,4-dimethyl-2-pentyne, 95% of the boron is placed at the less hindered position¹²²:

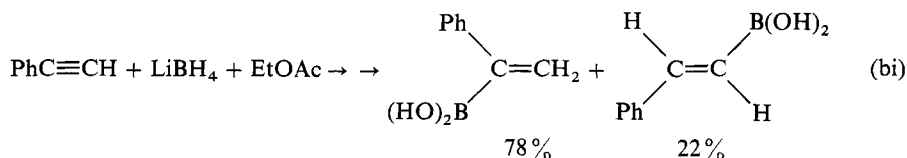


No dihydroboration occurs. The products are isolated by distillation and can be stored unchanged for long periods. Hydrolysis provides the corresponding alkenylboronic

acids. Approaches to alkenylboronic acid via hydroboration based on dicyclohexylborane, 4,4,6-trimethyl-1,3,2-dioxaborinane or 1-alkyl-1,2-azaborolidine are less convenient^{123,212}. The latter two reagents are poor hydroborating agents, reacting sluggishly even at elevated T. The dicyclohexylborane route requires a selective oxidation step²¹⁰:

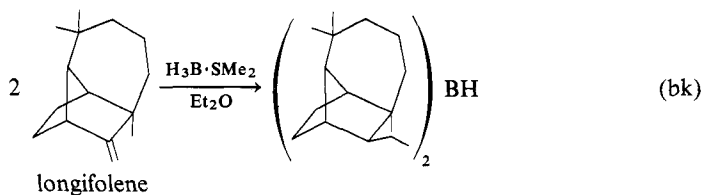
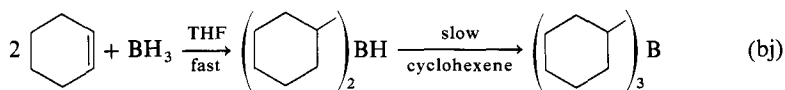


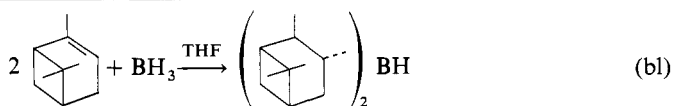
Alkenes and alkynes react with LiBH_4 in the presence of carboxylic acid esters to give dialkylborinates and alkenylboronates or dialkenylborinates, respectively, depending on the structure of the alkyne and the stoichiometry of the reagents²¹³. Regioselectivity of addition parallels that observed for other hydroborating agents. However, phenylacetylene reacts, placing the boron atom predominantly at the benzylic position:



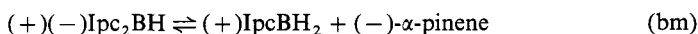
(iii) Organoboranes with Two B—C Bonds. The hydroboration of simple olefins with 2:1 $\text{H}_3\text{B}\cdot\text{THF}$ or $\text{H}_3\text{B}\cdot\text{SMe}_2$ proceeds rapidly beyond the dialkylborane stage as a result of a fast hydroboration of the alkene with the intermediate dialkylborane^{1-3,214,215}. An equilibrium mixture of the alkyldiboranes can be obtained via redistribution reactions; e.g., at 30°C, equilibrated tetraethylidiborane is composed²¹⁶ of 90% 1,1,2,2-tetraethylidiborane, 5% 1,1,2-triethylidiborane, and traces of Et_3B .

For trisubstituted olefins and certain hindered disubstituted olefins, e.g., cyclohexene and longifolene, hydroboration proceeds rapidly only to the dialkylborane stage. By careful control of conditions, the dialkylboranes can be obtained. In this way, certain important hydroborating agents, such as bis-3-methyl-2-butylborane³, dicyclohexylborane³, dilongifolylborane²¹⁷ and diisopinocampheylborane³, are synthesized:

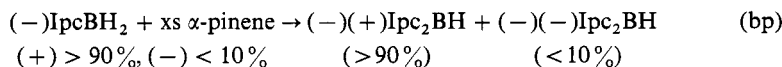
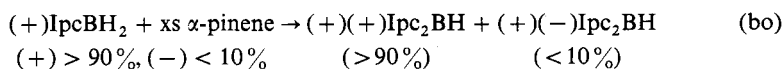
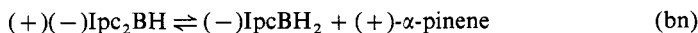




The latter two hydroborating reagents are chiral, and high optical purity is crucial for their effective application in asymmetric synthesis^{53–55}. α -Pinene with $\text{H}_3\text{B} \cdot \text{THF}$ proceeds quickly to the trialkyldiborane stage. The mixture attains equilibrium in 2–3 days at 0°C . The yield of Ipc_2BH depends on concentration and at 0.25 M is only 90%. Consequently, for efficient synthesis a higher concentration and *xs* α -pinene should be used; e.g., at 15% *xs* α -pinene and 1.0 M in THF, the yield is 99.5%. At 0°C , Ipc_2BH partially precipitates from THF with selective incorporation of the major enantiomer into the precipitate. Thus, Ipc_2BH obtained from (+)- α -pinene ($[\alpha]_{\text{D}}^{26} = +49.78^\circ$) of 97.4% optical purity gives, upon dehydroboration with Et_3N , (+)- α -pinene ($[\alpha]_{\text{D}}^{23.5} = +51.0$) of 99.8% optical purity. The formation of Ipc_2BH of higher optical purity than that of the starting α -pinene arises from preferential precipitation of (+)(+) Ipc_2BH over (+)(-) Ipc_2BH . The (+)(-) Ipc_2BH in the solution must undergo exchange with *xs* α -pinene containing 90% (+)- α -pinene²¹⁸:

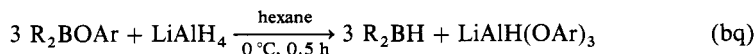


or

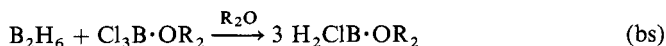


Both enantiomers of Ipc_2BH can be obtained starting either from (+)- or (–)- α -pinene. In an improved procedure, Ipc_2BH of high optical purity is obtained from $\text{H}_3\text{B} \cdot \text{SMe}_2$ and α -pinene of 92% optical purity by crystallization from THF²¹⁹. Other chiral dialkylboranes can also be upgraded in this way²²⁰. Chiral dialkylboronates²²¹ and borinates¹⁸⁸ are prepared using IpcBH_2 . *trans*-Disubstituted and trisubstituted olefins are hydroborated by this reagent with high asymmetric induction²²¹.

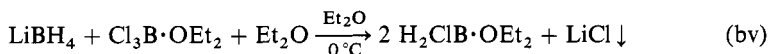
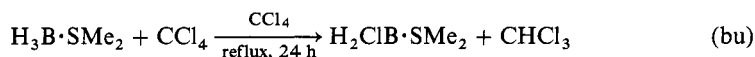
Alternatively, R_2BH can be synthesized by reduction of dialkylborinates, R_2BCl or R_2BBr with metal hydrides^{185,222–228}. They may be isolated by complexation with amines and released from these complexes by the addition of $\text{F}_3\text{B} \cdot \text{OEt}_2$ or stored as dialkylborohydrides¹⁸⁵. Otherwise, they must be utilized immediately to avoid disproportionation:



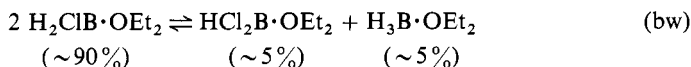
The starting dialkylhalogenoboranes and dialkylborinic acid esters can be obtained by hydroboration of olefins with monohalogenoboranes. The reagents are prepared by analogous methods as described for dihalogenoboranes^{85,198,199} or by^{229,230}:



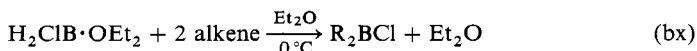
where X = Cl, Br, I;



Monochloroborane·etherate is most conveniently prepared by the last reaction^{3,85}. It exists in the solution in equilibrium with minor amounts of $\text{HCl}_2\text{B}\cdot\text{OEt}_2$ and $\text{H}_3\text{B}\cdot\text{OEt}_2$ ¹⁸⁹:



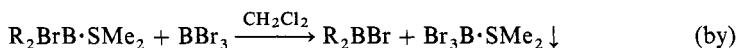
The reagent is stable in dilute ca 1 M ether. Concentration of such solutions results in disproportionation. The hydroboration of olefins with H_2ClB in THF is slow and incomplete²³¹. In the less basic solvents, Et_2O or diethyleneglycol dimethyl ether (diglyme), the reaction is fast and gives R_2BCl in high yield⁸⁵ (see Table 5):



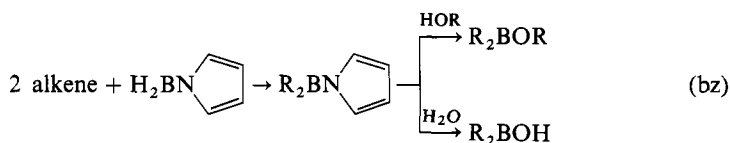
The isomeric purity of the R_2BCl is high, because a powerful directive effect operates.

The selectivity of addition of $\text{H}_2\text{ClB}\cdot\text{OEt}_2$ is influenced by electronic effects, whereas the steric factors are relatively small, similar to those observed in hydroborations with $\text{H}_3\text{B}\cdot\text{THF}$. Monochloroborane· SMe_2 shows the same selectivity but possesses advantages over the etherate. It is a liquid, stable at RT, available in a concentrated form and soluble in such solvents as CH_2Cl_2 , CHCl_3 , n-pentane and Et_2O . Monobromo- and monoiodoborane· SMe_2 complexes are similar. The reactivity toward alkenes decreases¹⁹⁵: $\text{H}_2\text{ClB}\cdot\text{SMe}_2 > \text{H}_2\text{BrB}\cdot\text{SMe}_2 > \text{H}_2\text{IB}\cdot\text{SMe}_2$. The regioselectivity of addition is shown in Table 6. The directive effects in these hydroborations are similar.

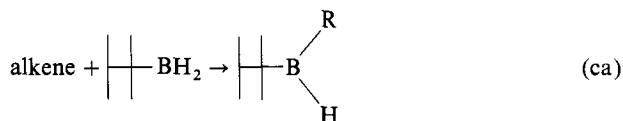
The hydroboration of olefins with $\text{H}_2\text{XB}\cdot\text{SMe}_2$ provides access¹⁹⁵ to R_2BX . Dialkylchloroboranes can be isolated by distillation; R_2BBr and R_2BI coordinate strongly with Me_2S , and these complexes, except for R_2BBr derived from hindered alkenes, do not dissociate completely during distillation to give products free from Me_2S . Pure products can be obtained by removing the Me_2S as the complex with BBr_3 or BI_3 :



The dialkylhalogenoboranes are transformed into the corresponding dialkylborinic acids and their esters by hydrolysis or alcoholysis. Dialkylpyrrolboranes are also used for this purpose⁴⁵:

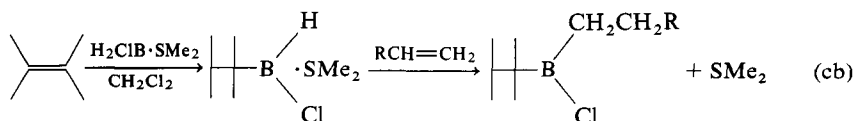


Dialkylboranes with two different alkyl groups and their derivatives can be obtained via hydroboration. Thus, 1:1 thexylborane hydroborates olefins at -20 to -25°C to give thexylmonoalkyl boranes¹⁷⁹:



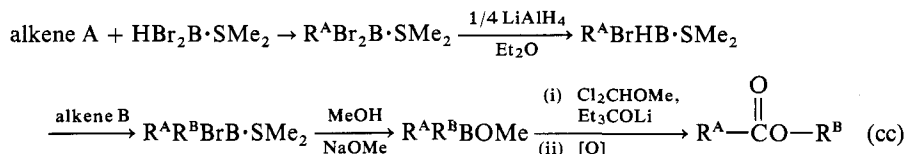
where R = i-Bu, s-Bu, norbornyl, trans-2-methylcyclohexyl.

The choice of only one alkyl group and the preferential dihydroboration of monosubstituted 1-alkenes are limitations. Thexylchloroborane·SMe₂ offers a solution to the latter problem. This reagent hydroborates reactive olefins, such as terminal or unhindered disubstituted alkenes, quantitatively and regioselectively, in CH₂Cl₂, ClCH₂CH₂Cl, Et₂O and THF to give the corresponding thexylalkylchloroboranes^{86,232–234}:



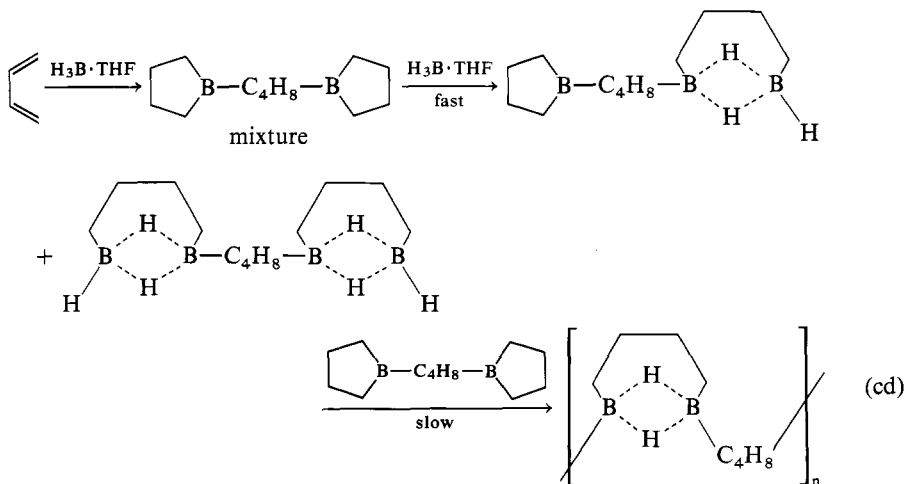
However, with less reactive olefins, such as cyclohexene, 1-methylcyclohexene or α -pinene, redistributed products are formed owing to preequilibration of the reagent. Regioselectivity of ThxHCIB·SMe₂⁸⁶ is comparable to that of H₂ClB·OEt₂ and some times even to 9-BBN. Thexylalkylchloroboranes, unlike thexylalkylboranes, are stable and can be stored for prolonged periods. By hydridation with K[HB(OPr-i)₃] they are transformed into thexylalkylboranes²³². Hydroboration of alkenes with this reagent provides thexylalkenylhaloboranes²³³.

The reduction-hydroboration of alkyl dihalogenoboranes provides a more general approach to unsymmetrical dialkylboranes. The reduction of RBX₂ (X = Br, Cl) with LiAlH₄ followed by the addition of a terminal olefin gives RR'BX. Redistribution does not occur, as proved by clean conversion of these dialkylhalogenoboranes into ketones via DCME reaction. However, if the olefin is present in the reaction mixture prior to the reduction, redistributed products are formed²⁰²:



This procedure also works for alkynes^{235,236}.

Cyclic dialkylboranes are prepared¹⁴ by hydroboration of dienes with 1:1 $\text{H}_3\text{B} \cdot \text{THF}$. Trifunctional boranes give with difunctional dienes polymeric organoboranes. Fortunately, these products can be transformed into monomers or dimers by further reaction. Thus, the hydroboration product obtained from 1,3-butadiene is polymeric²³⁷⁻²⁴⁰. The initial products, which are dumbbell-shaped organoboranes, are cleaved by the remaining borane to give the polymer.



The hydroboration of 1,4-pentadiene is similar²⁴¹. The product is 70:30 polymeric organoborane and borinane along with a trace of 2-methylborolane. In contrast, the

TABLE 7. SYNTHESIS OF CYCLIC DIALKYLBORANES VIA HYDROBORATION OF DIENES WITH $\text{BH}_3 \cdot \text{THF}$ IN 1:1 RATIO

Diene	% Yield of boracycloalkane	Product	Distribution (%)
1,3-Butadiene ^a	0	—	
1,4-Pentadiene ^b	30	borinane	83
		2-methylborolane	17
1,5-Hexadiene ^c	78	borepane	70
		2-methylborinane	30
2,4-Dimethyl-1,4-pentadiene ^d	89	3,5-dimethylborinane	99
		unidentified product	1
2,5-Dimethyl-1,5-hexadiene ^d	75	3,6-dimethylborepane	91
		unidentified product	9
1,7-Octadiene ^e	0	—	
1,4-Cyclohexadiene ^e	0	—	
1,5-Cyclooctadiene ^e	91	9-borabicyclo[3.3.1]nonane	72
		9-borabicyclo[4.2.1]nonane	28
4-Vinylcyclohexene ^e	12	at least three products	
D-(+)-Limonene ^e	25	at least four products	

^a Ref. 254.

^b Ref. 255.

^c Ref. 256-260.

^d Ref. 261.

^e Ref. 262.

hydroboration of 1,5-hexadiene, 2,4-dimethyl-1,4-pentadiene and 2,5-dimethyl-1,5-hexadiene is cyclic in ca. 78%, 90% and 75%, respectively^{242,247} (see Table 7). These hydroborations, at least when carried out in a borane-to-diene addition mode, proceed via the formation of dumbbell-shaped organoboranes. For 1,3-butadiene and 1,4-pentadiene, these initially formed organoboranes contain borolane rings not stable to the action of borane. The other dienes produce dumbbell-shaped organoboranes with six- or seven-membered rings undergoing B-alkyl bond cleavage instead of the ring opening in the reaction with borane. The reactivity order of B—C bonds toward $\text{H}_3\text{B}\cdot\text{THF}$ is¹⁴:

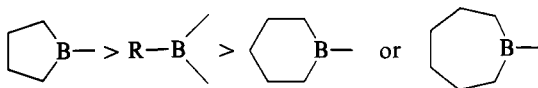
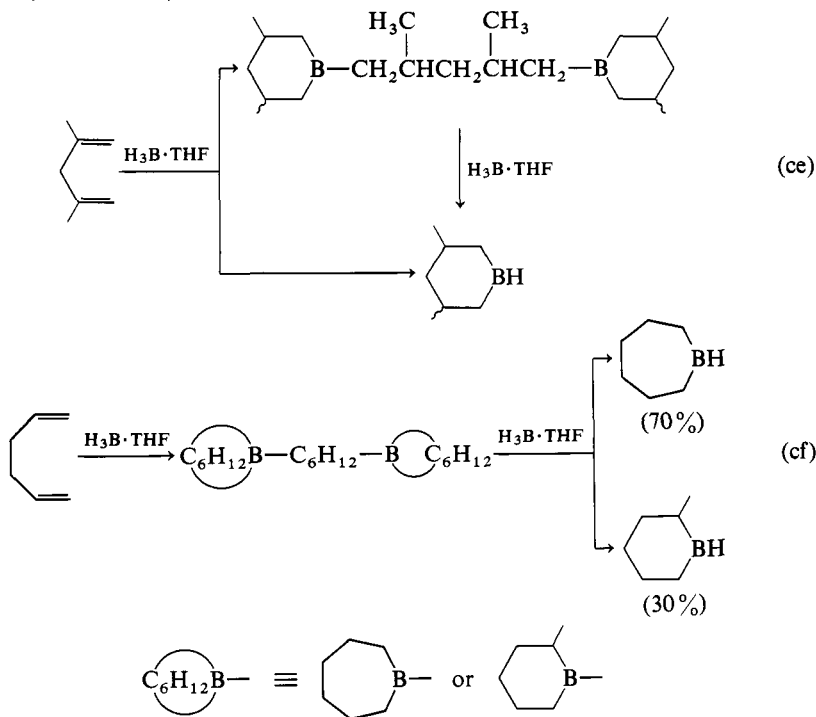
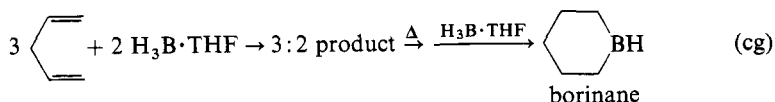


Figure 8.

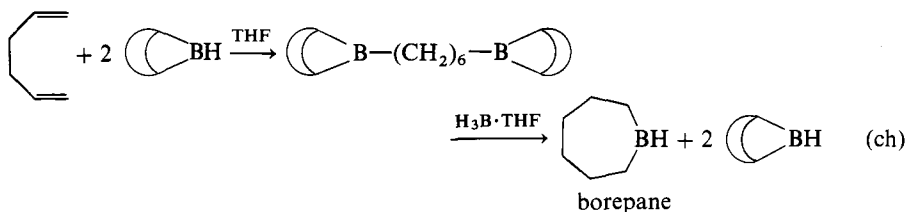
Consequently, the hydroboration of 2,4-dimethyl-1,4-pentadiene, which is also representative for 1,5-hexadienes, is:



Convenient procedures are available for isomerically uncontaminated borinane which can be obtained by the hydroboration of 1,4-pentadiene in a 3:2 ratio, followed by thermal isomerization and exchange with borane²⁴¹:

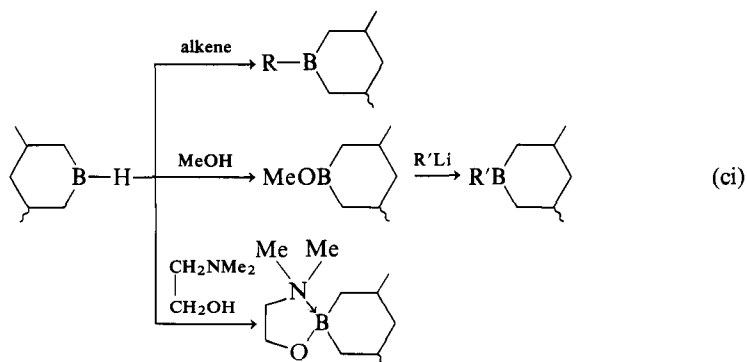


Alternatively borinane and borepane are obtained^{243–245} by hydroboration of 1,4-pentadiene and 1,5-hexadiene, respectively, with 9-BBN followed by exchange with $\text{H}_3\text{B} \cdot \text{THF}$ or $\text{H}_3\text{B} \cdot \text{SMe}_2$:

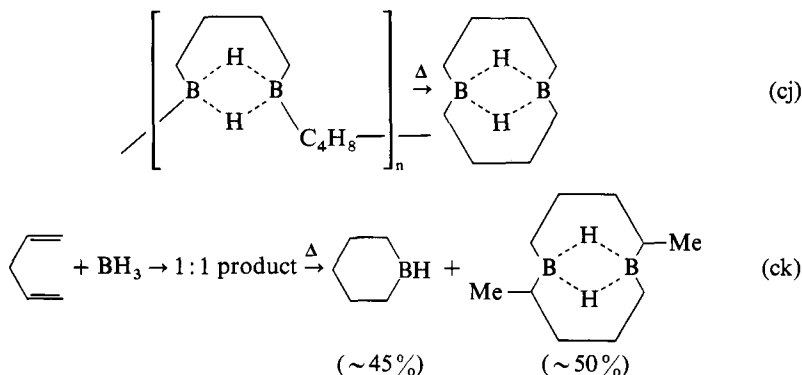


Borinanes with Si or Ge in the ring are obtained similarly²⁴⁶.

Borinanes and borepanes are valuable hydroborating agents. Unlike other R_2BH with primary alkyl groups, they do not redistribute. The hydroboration of alkenes provides B-alkylboracyclanes useful in free-radical reactions of organoboranes. Methanolysis gives B-alkoxyboracyclanes, which may be further utilized in transmetallation reactions with alkyllithium or organomagnesium halide reagents to synthesize derivatives not available by direct hydroboration^{3,247}:



The polymeric organoboranes derived from 1,3-butadiene and 1,4-pentadiene are transformed by thermal treatment into transannular bridged structures, 1,6-diboracyclodecane and 2,7-dimethyl-1,6-diboracyclodecane, respectively^{241,248–250}:



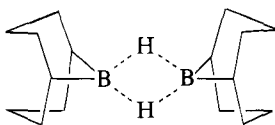
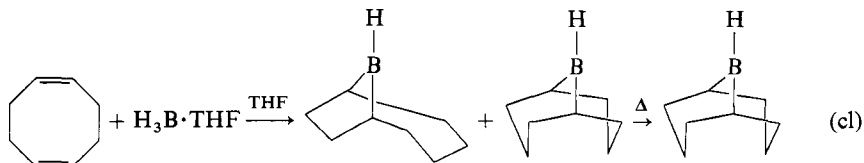


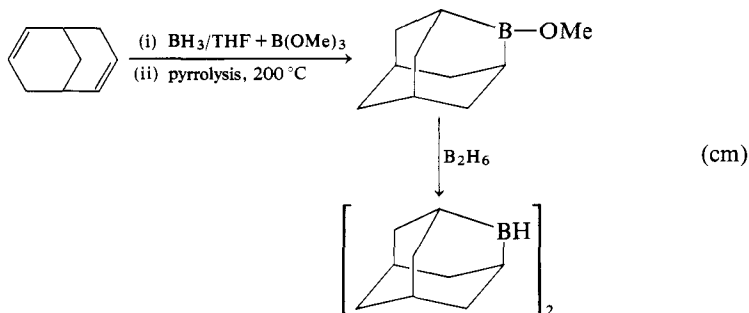
Figure 9.

1,6-Diboracyclodecane, also formed from thermally unstable bis-borolane²⁵¹, possesses unusual properties for a dialkylborane. It does not react with olefins at appreciable rates at 100°C and is stable to hydrolysis or methanolysis at 25°C. Apparently, the transannular bridge incorporated in the ring is inaccessible to reagents that attack B—H bonds with ease. It hydroborates 2-methyl-1,3-butadiene in refluxing toluene to yield the dumbbell-shaped organoborane; however, predissociation to borolane does not occur²⁵².

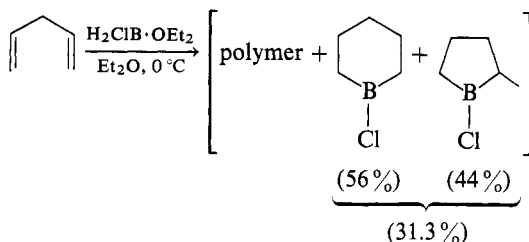
1,7-Octadiene and higher α,ω -dienes with 1:1 $\text{H}_3\text{B}\cdot\text{THF}$ leads to polymeric material. Low yields of cyclic products are also obtained in the hydroboration of mixed dienes, e.g., 4-vinylcyclohexene or limonene (see Table 7), but 1,5-cyclooctadiene undergoes cyclic hydroboration in high yield. A mixture of 9-borabicyclo[3.3.1] nonane (9-BBN) and 9-borabicyclo[4.2.1]nonane is formed. Other intermediates are also observed by B NMR²⁵³. Upon heating, the latter compound is transformed^{3,80,83,254} to the more thermodynamically stable 9-BBN:



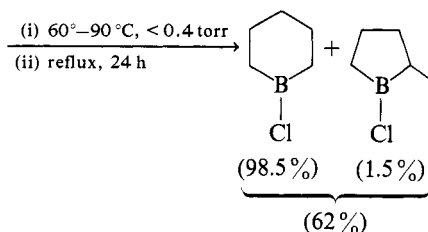
The thermal stability of 9-BBN is remarkable. It distills without dissociation to the monomer at 195°C and 12 torr (16 Pa)⁸³. However, partial thermolysis occurs on heating at 170°C for 72 h²⁵⁵. It is dimeric in the solid²⁵⁶ and in solvents, such as CCl_4 , hexane, benzene and Et_2O ⁸³ (see Fig. 9). In THF and Me_2S , an equilibrium between $(9\text{-BBN})_2$ and solvent-complexed 9-BBN monomer $9\text{-BBN}\cdot\text{THF}$ or $9\text{-BBN}\cdot\text{SMe}_2$ exists^{155,157,254}. Among the hydroborating agents, 9-BBN is of high regio- and stereoselectivity¹³³. It is readily methanolized to B-methoxy-9-BBN—a useful intermediate in the synthesis of 9-BBN derivatives. Hydroboration of bicyclo[3.3.1]nona-2,6-diene in the presence of $(\text{MeO})_3\text{B}$, followed by pyrolysis and exchange with diborane, affords 2-boraadamantane²⁵⁷:



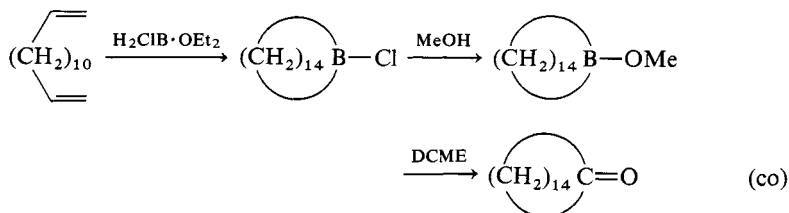
Beside $\text{H}_3\text{B}\cdot\text{THF}$ or $\text{H}_3\text{B}\cdot\text{SMe}_2$, difunctional hydroborating agents are well suited for cyclic hydroboration of dienes. B-Halogenoboraheterocycles can be synthesized using monohalogenoboranes^{258,259}. The initial products in the hydroboration of acyclic α,ω -dienes with $\text{H}_2\text{ClB}\cdot\text{OEt}_2$ are only partly cyclic for 1,4-pentadiene and 1,5-hexadiene and polymeric for higher dienes. The polymeric organoboranes depolymerize when heated under vacuum to give B-chloroboracycloalkanes:



(cn)



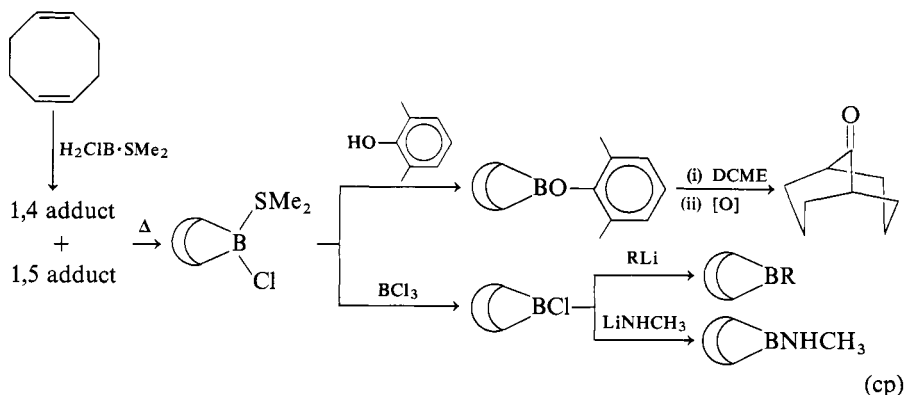
Pure B-chloro-substituted borinane, borepane and 3,6-dimethylborepane are obtained in this way²⁵⁸. 1,6-Heptadiene gives the eight-membered B-chloroborocane, although some isomerization to six- and seven-membered boracycloalkanes occurs during distillation-depolymerization. Pyrolysis of B-chloroorganoboranes derived from higher α,ω -dienes results in thermal isomerization, and a mixture of substituted B-chloroboracycloalkanes with five- to seven-membered rings is formed. Under high dilution such dienes are transformed into large ring boraheterocycles in low yields²⁵⁸:



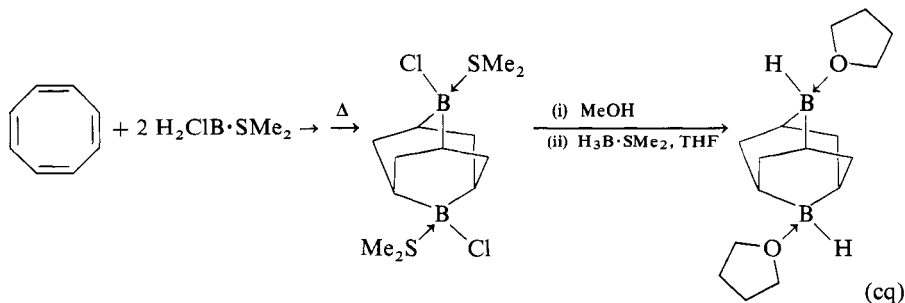
where $\text{DCME} = \text{Cl}_2\text{CHCOCH}_3$.

A simple, convenient synthesis of B-halogeno-9-borabicyclo[3.3.1]nonane and its [4.2.1] isomer is realized by the hydroboration of 1,5-cyclooctadiene with monohalogenoboranes²⁶⁰. The thermodynamically less stable [4.2.1] isomer, predominating in the mixture initially formed, can be converted to the more stable B-X-9-BBN by gentle

heating. The B-X-9-BBN compounds are useful synthetic intermediates, providing access to other 9-BBN derivatives and the bicyclo[3.3.1]nonane system²⁶⁰:

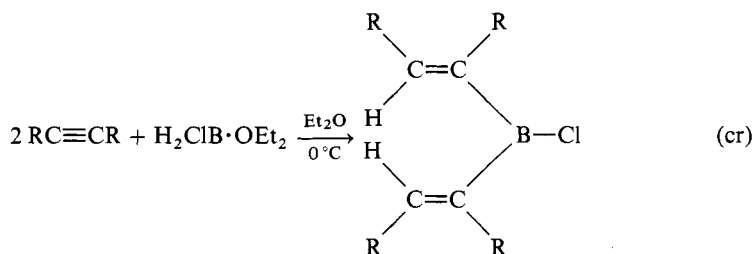


The symmetrical cage-like structure of 2,6-dichloro-2,6-diboraadamantane is formed in a two-step hydroboration-depolymerization from cyclooctatetraene and $\text{H}_2\text{ClB}\cdot\text{SMe}_2$. Methanolysis, followed by redistribution with $\text{H}_3\text{B}\cdot\text{SMe}_2$, gives 2,6-diboraadamantane²⁶¹:

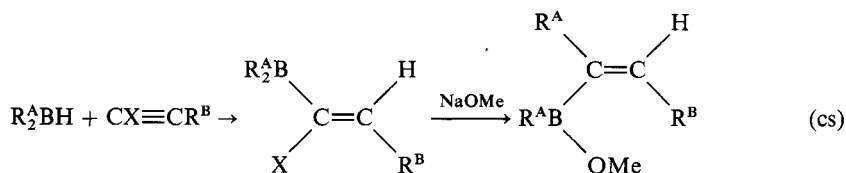


The THF bis adduct can be crystallized. The electron-pair acceptor acid properties of the boron atoms must be enhanced in this structure; the structurally similar 9-BBN does not coordinate as strongly with THF. Strong complexation of THF is also observed in 1-boraadamantane^{262,263}.

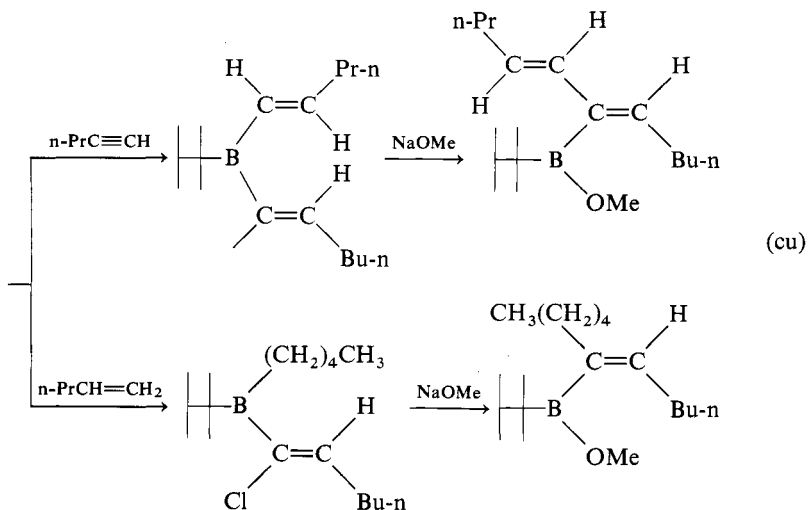
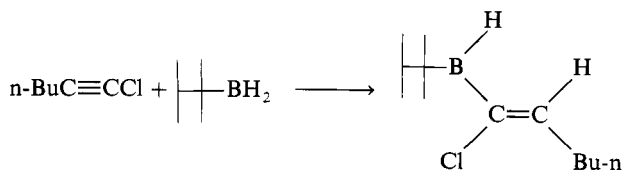
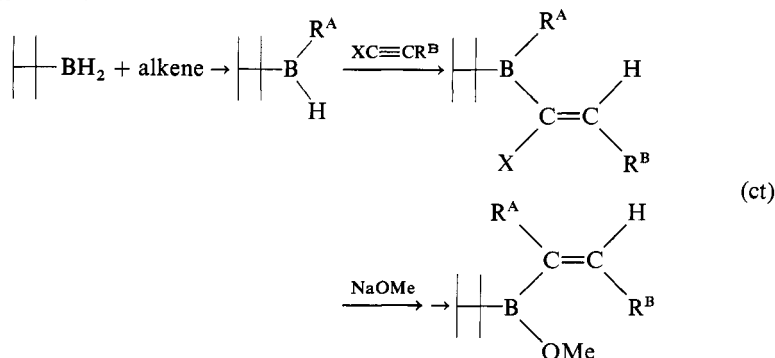
Alkynes monohydroborate with $\text{H}_2\text{ClB}\cdot\text{OEt}_2$ to give symmetrical dialkenylchloroboranes. Internal alkynes react in a stoichiometric ratio, whereas 30–40% xs of the terminal alkyne must be used to avoid competing dihydroboration⁸⁵:



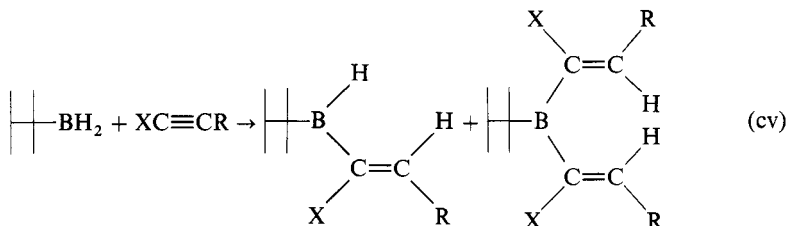
Alkylalkenylborane derivatives can be obtained by hydroboration of 1-halo-1-alkynes with dialkylboranes, followed by the base-induced migration of an alkyl group from boron to the adjacent carbon atom^{10,264}:



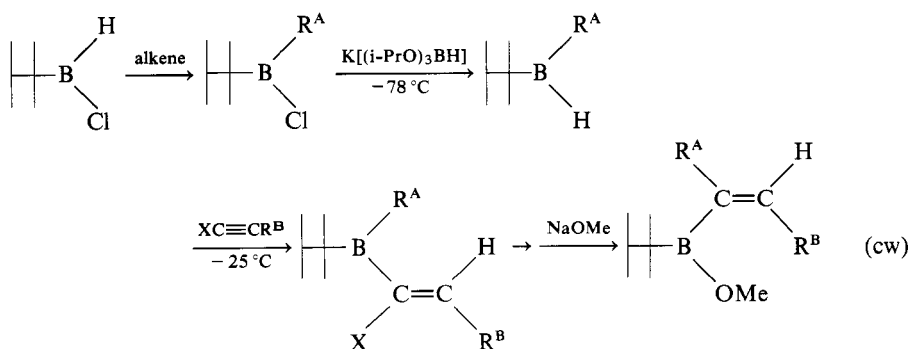
Alkenylthexylborane derivatives are prepared similarly, starting with
thexylborane^{265,266}:



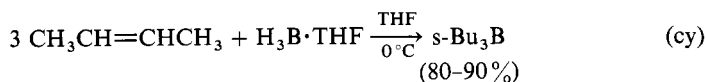
However, the scope of the first approach [Eq. (ct)] is limited by the availability of suitable thexylmonoalkylboranes, which are formed cleanly only from alkenes with intermediate steric requirements. The second method [Eq. (cu)] suffers from low yields of the xylalkenylboranes owing to competing dihydroboration of thexylborane:



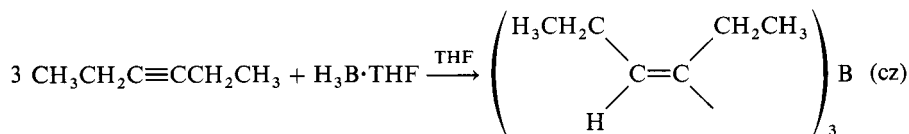
A more convenient procedure is based on thexylchloroborane. Hydroboration of an alkene gives thexylalkylchloroborane, which in turn is reduced to thexylmonoalkylborane, subsequently hydroborating 1-halo-1-alkyne^{267,268}:



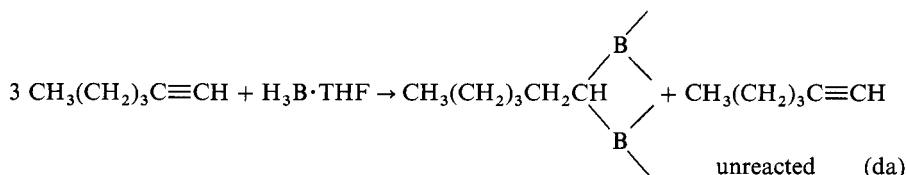
(iv) Organoboranes with Three B—C Bonds. Hydroboration is a route to trialkyl- and alkylalkenylboranes. Procedures, reactivity and directive effects are given in §5.3.2.5.1.(i). Alkenes are transformed into the corresponding symmetrical R_3B by $\text{H}_2\text{B}\cdot\text{THF}$. It is the reagent of choice for such syntheses whenever the appropriate alkene is available¹⁻³:



For most transformations, the product is pure enough to be used directly without isolation. Trialkenylboranes can be obtained in moderate yields by hydroboration of internal alkynes²⁶⁹:

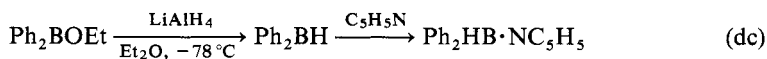


However, competing dihydroboration also occurs, becoming the predominant mode of reaction with terminal alkynes:

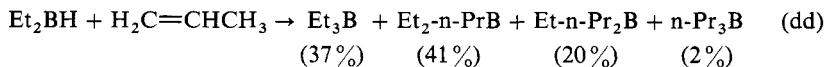


Although $\text{H}_3\text{B}\cdot\text{THF}$ is an excellent hydroborating agent, its trifunctionality limits its applicability. Thus, sterically hindered alkenes are hydroborated only to the mono- or dialkylborane stage. Controlled, stepwise hydroboration of structurally different olefins is rarely possible. Regioselectivity in hydroboration of internal disubstituted alkenes and alkynes is low. Monohydroboration of acyclic dienes cannot be achieved owing to competing dihydroboration. Trialkylboranes sometimes only utilize one group³, and consequently symmetrical R_3B may at best react in 33 % yield. Finally, in the hydroboration of terminal alkenes with $\text{H}_3\text{B}\cdot\text{THF}$, 6% of the boron is placed at the secondary position. This may lead to isomeric products in such reactions as free-radical displacements, in which secondary alkyl groups are transferred preferentially to primary groups³.

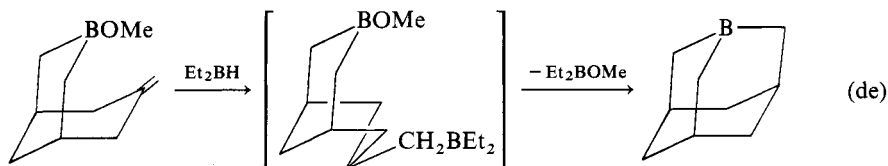
These difficulties can be circumvented by application of alkyl- or aryl-substituted boranes as hydroborating agents. The reagents are obtained either by partial hydroboration of hindered alkenes [Eqs. (ae), (af), (bj)–(bl)] or by other methods, e.g., redistribution^{7,9,17,270–272} or reduction^{202,222–228}:



Lower dialkylboranes are reactive and hydroborate alkenes rapidly, even without a solvent below 0°C . The reactivity depends on the alkyl group, decreasing²⁷²: primary > secondary > cyclo-alkyl. Regioselectivity approaches that of R_2BH with bulky substituents. Unfortunately, mixtures of products are formed because the reagents disproportionate and are in equilibrium with R_3B and alkylated diboranes²⁷²:



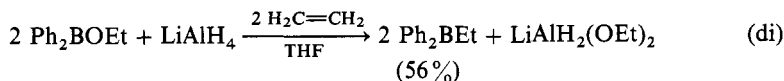
Such mixtures disproportionate in the presence of catalytic amounts of boranes, alanes or R_3Al . By removing the lowest bp R_3B , the equilibrium may be shifted to one side, providing the symmetrical R_3B in high yield and purity²⁷². Despite these inconveniences, lower R_2BH can be used for the synthesis of R_3B when the thermal treatment does not affect the final product²⁷³:



Several methods for the synthesis of unsymmetrical trialkylboranes are based on the in situ generation of the dialkyl- or diarylborane, which is trapped by an olefin prior to disproportionation^{202,223–228,268}:

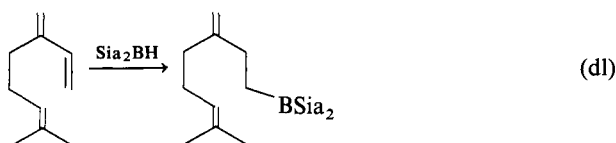
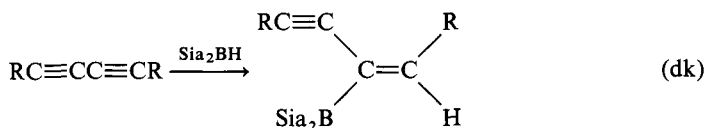
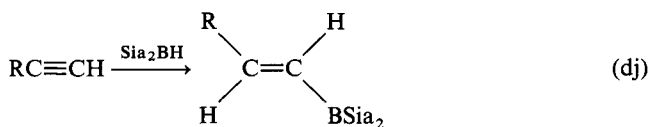


where M = Na, K, Li;



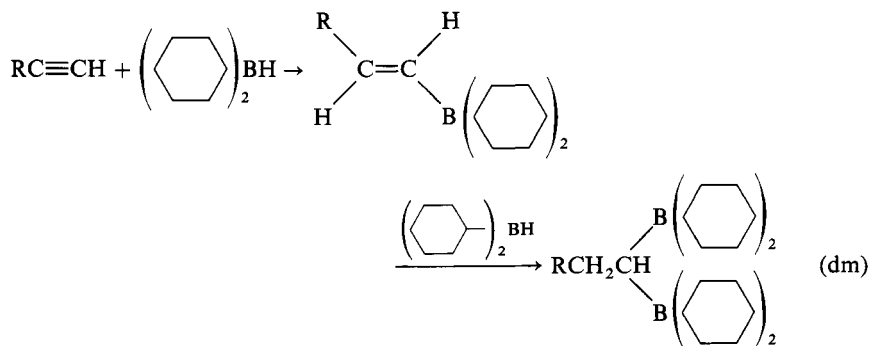
Dialkylboranes with bulky alkyl groups do not disproportionate so readily and hydroborate alkenes of lower steric hindrance than the parent alkene to give the corresponding unsymmetrical trialkylboranes in high yield and purity. Bis(3-methyl-2-butyl)borane is one such reagent, synthesized by controlled hydroboration of 2-methyl-2-butene³.

The bulky alkyl groups impose a high degree of regioselectivity in hydroboration, which is controlled primarily by steric factors; e.g., in the hydroboration of aliphatic monosubstituted 1-alkenes and styrene, 99% and 98% of boron is placed at the terminal positions⁸⁴, respectively, compared to 94% and 81% for $H_3B \cdot THF$ ^{1,81}. The reactivities of structurally different alkenes vary over 10^4 (see Table 3), and advantage can be taken of this in the synthesis of alkenylboranes and selective hydroboration of difunctional systems^{269,274–276}:

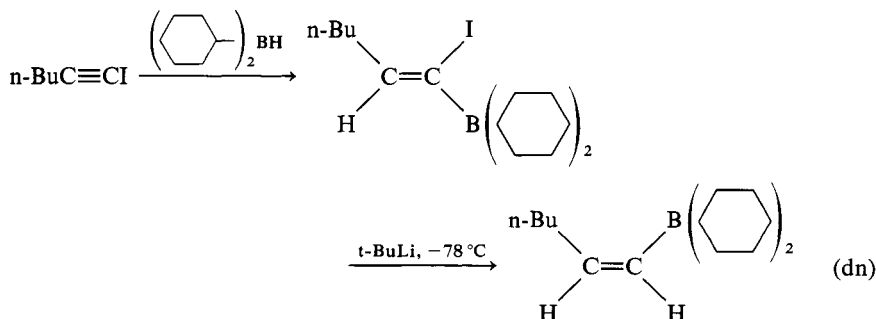


A limitation of Sia_2BH is the low thermal stability of both the reagent and the organoboranes derived from it. Dicyclohexylborane showing similar hydroboration characteristics often substitutes for Sia_2BH . In applications requiring thermal treatment

of organoboranes, it is superior to $\text{Si}\alpha_2\text{BH}$, because the cyclohexyl groups are not affected by T. The reagent is sterically less demanding and more reactive than $\text{Si}\alpha_2\text{BH}$. Consequently, hydroboration of alkynes can be controlled to proceed either to alkenyldicyclohexylboranes or to gem-dibora derivatives^{99,277}:

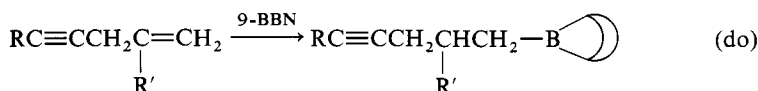


Dimesitylborane is highly selective in the hydroboration of substituted alkynes and can be used for the syntheses of alkenyldimesitylboranes²⁷⁸. Dicyclohexylborane and $\text{Si}\alpha_2\text{BH}$ are applied in the synthesis of cis-alkenyloboranes not available by direct hydroboration^{105,279,280}:

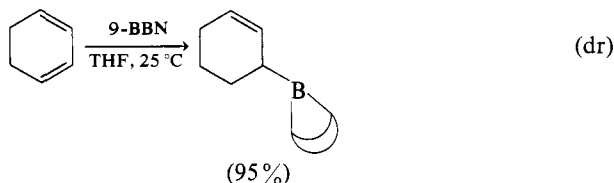
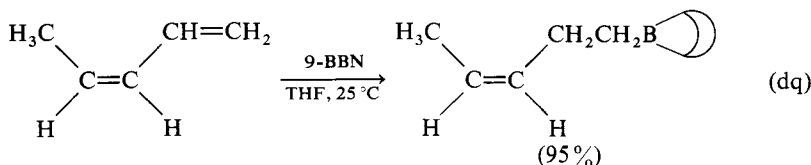
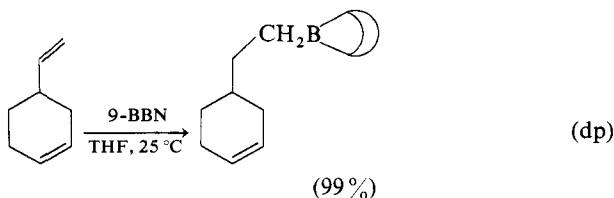


9-Borabicyclo[3.3.1]nonane (9-BBN) is a particularly valuable hydroborating agent of remarkable stability and high regio- and stereoselectivity³. It is a crystalline solid, stable indefinitely at RT in the absence of air and moisture. Hydroborations with 9-BBN can be performed in hexane, benzene, dichloromethane, Et_2O or THF. In THF the reaction proceeds faster than in the other solvents; however, internal alkenes require many hours for complete hydroboration at RT. Consequently, for preparative purposes the reaction is carried out in refluxing THF. Under these conditions, even hindered alkenes, e.g., 2,3-dimethyl-2-butene, react in 1 h. Fortunately, the B-alkyl-9-BBN derivatives are resistant to thermal isomerization. Thus, B-3-hexyl-9-BBN requires heating at 150°C for 168 h to attain the equilibrium distribution of boron along the hexyl chain¹³⁴. At that T, the isomerization of tri-3-hexylborane is complete in 1 h. Advantage of this resistance can be taken in the synthesis of certain thermally labile systems; e.g., the hydroboration of 1-methylcyclooctene with either $\text{H}_3\text{B}\cdot\text{THF}$ or $\text{Si}\alpha_2\text{BH}$ gives a mixture of products with boron distributed around the ring, whereas 9-BBN provides B-trans-2-methylcyclooctyl-9-BBN of 98% purity^{133,134}.

The openness of the strained 9-BBN molecule makes possible hydroboration of even hindered alkenes not readily attacked by Si_2BH . This indicates a lower degree of steric control in the reaction with 9-BBN, but 9-BBN is more sensitive to electronic effects, e.g., the difference in reactivity between *p*-trifluoromethylstyrene and *p*-methoxystyrene is 1.5 for Si_2BH and 67 for 9-BBN¹¹⁵. The relative reactivities of alkenes toward 9-BBN vary over 10^5 (see Table 3). A high preference for hydroboration of terminal double bonds and a small difference in the reactivity of *cis-trans* pairs is evident. Unlike other hydroborating agents, 9-BBN reacts faster with terminal double bonds than with internal triple bonds²⁸¹; e.g.:

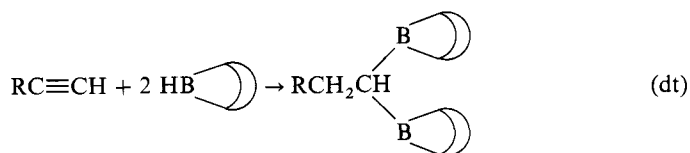
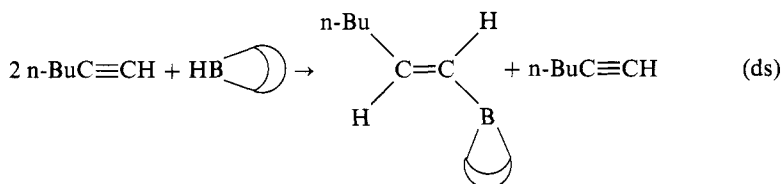


where if $\text{R} = \text{n-Pr}$, n-Hex or Ph , then $\text{R}' = \text{H}$; if $\text{R} = \text{n-Hex}$, $\text{R}' = \text{Me}$. Selective hydroboration of dienes can also be achieved^{282–284}. Isolated dienes behave like alkenes of similar substitution, reacting according to the reactivity difference of such alkenes. Conjugated dienes are less reactive in hydroboration than the isolated double bonds. Consequently, the unsaturated organoboranes initially formed react faster than the diene and dihydroboration occurs, e.g., in the reaction of 1,3-cycloheptadiene, and 1,3-cyclooctadiene with 9-BBN and other hydroborative agents^{283,284}. However, certain conjugated dienes, e.g., 1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene, undergo selective hydroboration to give either B-homoallylic or B-allylic-9-BBN derivatives, depending on the substitution of the diene system:

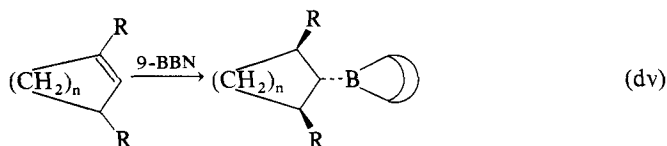
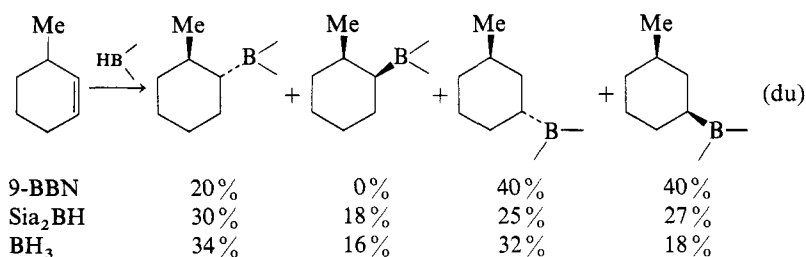


The monohydroboration of internal alkynes is achieved with a 100% xs of the terminal alkyne to prevent the competing dihydroboration⁸⁷. The B-alkenyl-9-BBN

derivatives are stable and can be isolated by distillation. They are more reactive than ordinary alkenyl boranes, undergoing addition to aldehydes²⁸⁵. Addition of 2 equiv of 9-BBN to 1-alkyne produces 1,1-diboraalkanes in excellent yield^{3,87,100}:



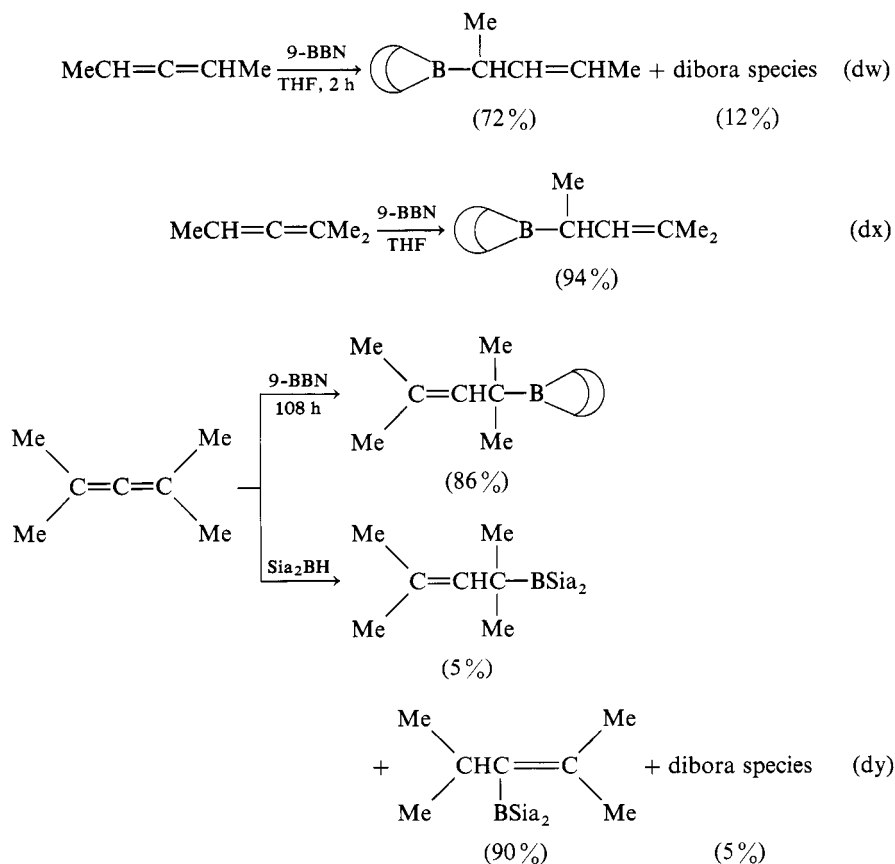
Highest regio- and stereoselectivity among all boranes is exhibited by 9-BBN. Terminal alkenes are transformed into the corresponding B-alkyl-9-BBN derivatives in purities approaching 100%. Unsymmetrically disubstituted alkynes and alkenes also react selectively^{82,83,87}. Addition to 3-methylcyclohexene and 3-methylcyclopentene gives no cis-1,2-isomer¹³³. 1,3-Dialkylcycloalkenes are transformed into single stereo isomers²⁸⁶:



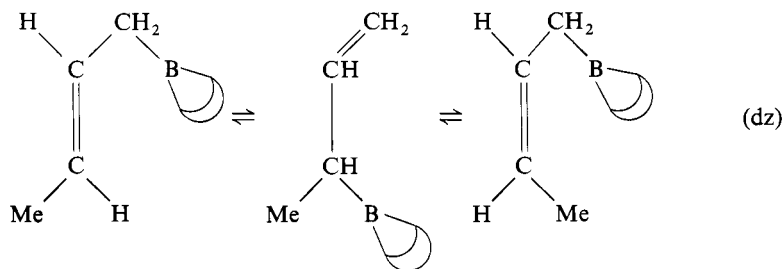
where $n = 1, 2, 3$.

In contrast to $\text{H}_3\text{B} \cdot \text{THF}$ and other dialkylboranes, 9-BBN shows a strong tendency to form B-allylic-9-BBN derivatives in the hydroboration of aliphatic allenes. This tendency is retained even when the allene system is unfavorably substituted. Lower selectivity may be expected for cyclic allenes, for 1,2-cyclononadiene gives 17% of B-cyclononen-1-yl-9-BBN and 83% of B-cyclononen-2-yl-9-BBN. The reaction can be

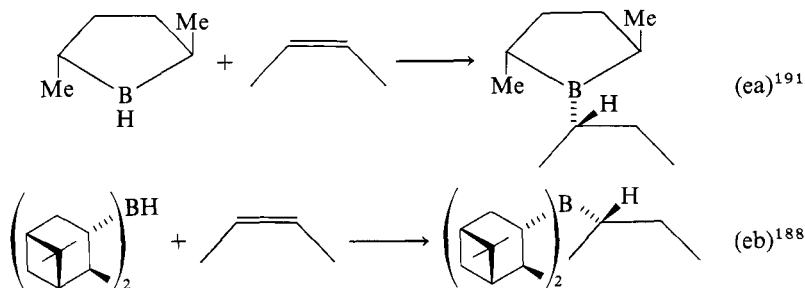
stopped at the monohydroboration stage. Only propadiene undergoes extensive dihydroboration²⁸⁷:



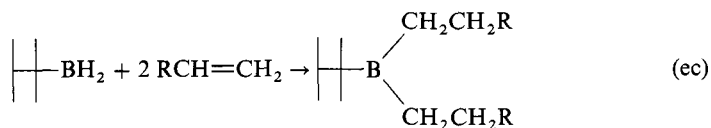
Two allylic organoboranes might be expected in the hydroboration of unsymmetrically substituted allenes. However, only one, possessing the boron atom at the least substituted site, is formed. This may not reflect solely the initial position of boron attack on the allene, because allylic boranes undergo permanent allylic rearrangement^{288,289}. In the equilibrium, the boron atom favors the least substituted position:



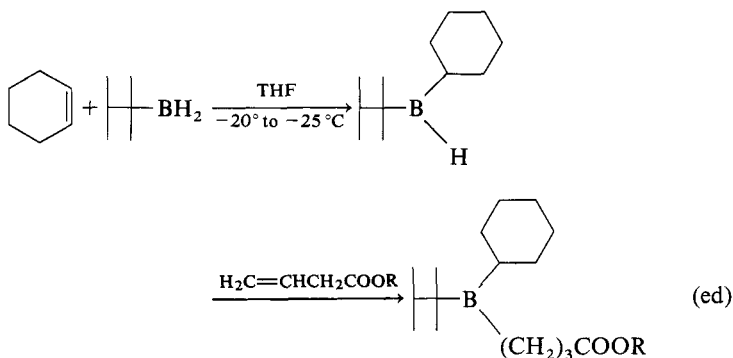
Chiral trialkylboranes which are important synthetic intermediates are available by hydroboration of olefins with dialkylboranes:^{54,219,290–292}



2,3-Dimethyl-2-butylborane (thexylborane) is a valuable reagent for the synthesis of unsymmetrical trialkyl- and alkylalkenylboranes. It has only a limited stability, undergoing slow thermal isomerization (91% in 16 days at 25°C), and loses 2,3-dimethyl-2-butene on standing³. For these reasons, it should be prepared and used fresh. Alternatively, it may be stabilized by complexation with *N,N*-diethylaniline²⁹³. The complex is stable at 0°C for long periods and is miscible with hexane, benzene, CH₂Cl₂ and ethers. Despite the bulky thexyl group, the reagent reacts with alkenes of lower steric hindrance than 2,3-dimethyl-2-butene²⁹⁴. The directive effect in the hydroboration of alkenes with thexylborane parallel those with H₃B·THF. Hydroboration of 1-alkenes proceeds readily to the corresponding thexyldialkylboranes:

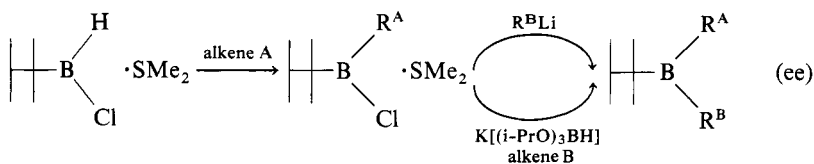


With moderately hindered alkenes, e.g., cyclohexene, 2-methyl-2-butene, isobutene, norbornene, etc., the reaction can be stopped at the thexylmonoalkylborane stage¹⁷⁹. Subsequent addition of an unhindered alkene gives mixed trialkylboranes²⁹⁵:

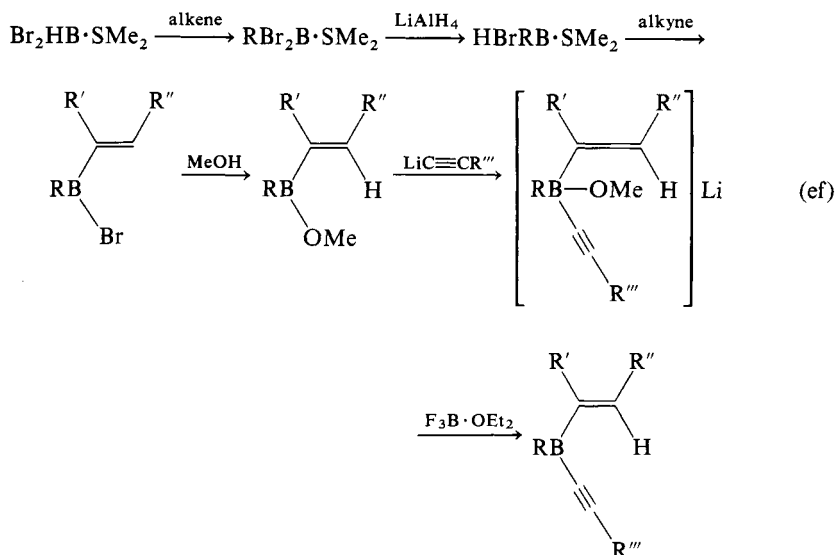


A more general approach allowing the introduction of two primary alkyl groups into the product starts with thexylchloroborane. Hydroboration of an alkene gives

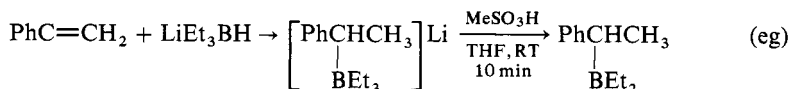
thexylalkylchloroborane, which is transformed into the R_3B , either by displacement of Cl with the organolithium reagent or by reduction–hydroboration^{232,233}:



A general synthesis of mixed trialkylboranes²⁰² and alkylalkenylalkynylboranes²³⁵ is based on a hydroboration–reduction sequence starting with dihalogenoborane:

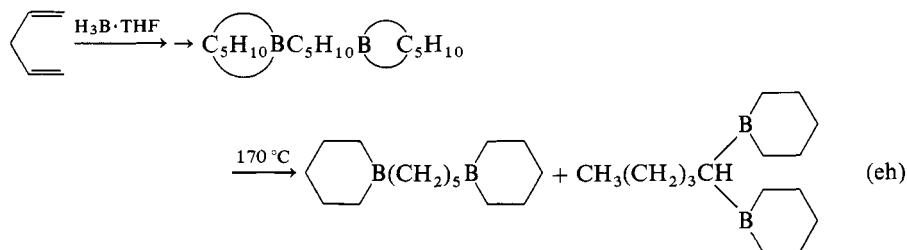


Alkyldiethylboranes are obtained by the addition of lithium triethylborohydride to substituted styrenes²⁹⁶. The hydrogen adds to the carbon containing the most hydrogen:

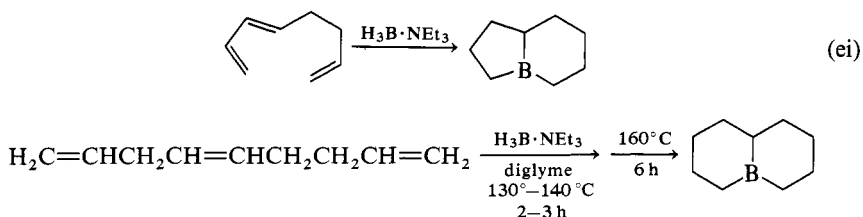


Two equivalents 1-alkyne with thexylborane produces the thexyldialkenylboranes²⁹⁷. Thexylalkylalkenylboranes can be obtained either by sequential hydroboration of an alkene–alkyne pair with thexylborane [Eq. (ct)] or via hydroboration of an alkene with thexylchloroborane, followed by reduction and hydroboration of an alkyne [Eq. (cw)]. Cyclic trialkylboranes are synthesized via hydroboration. Thus, $\text{H}_3\text{B} \cdot \text{THF}$ reacts 2:3 with simple acyclic dienes to give predominantly the dumbbell-shaped organoboranes. When heated, they undergo isomerization to the more thermodynamically stable isomers. These empirical rules predict their thermal behavior²⁴¹: (a) the thermal

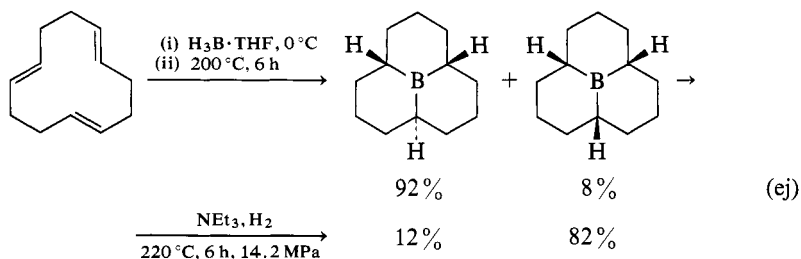
isomerization of the ring moieties present in the 2:3 dumbbell-shaped compounds proceeds to form predominantly six-membered rings when possible; (b) the thermal isomerization of the chain moieties present in the 2:3 dumbbell compounds proceeds to form predominantly α,α - and α,ω -diboraalkane moieties:



Hydroboration of acyclic trienes with 1:1 $\text{H}_3\text{B} \cdot \text{THF}$ at 0°C leads to insoluble products. Monomeric bicyclic boranes are produced in low yields. These organoboranes are obtained, however, either by thermal treatment of the insoluble products or directly by hydroboration of trienes with borane-triethylamine complex²⁹⁸.

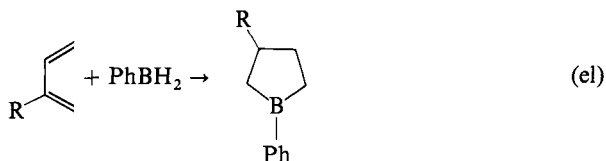
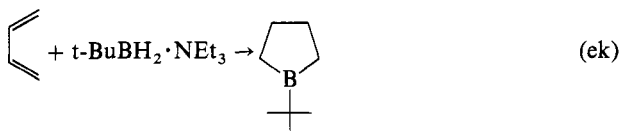


Similarly, hydroboration of trans,trans,trans-cyclododecatriene with equimol $\text{H}_3\text{B} \cdot \text{THF}$ at 0°C gives a polymeric product. Its thermal treatment produces cis,trans- and cis,cis-perhydro-9b-boraphenalenenes in 92:8 ratio. Hydroisomerization of this mixture at 220°C in the presence of triethylamine leads to an equilibrium mixture of cis,trans- and cis,cis-perhydro-9b-boraphenalenenes (12:82)²⁹⁸:



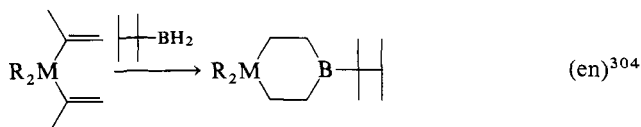
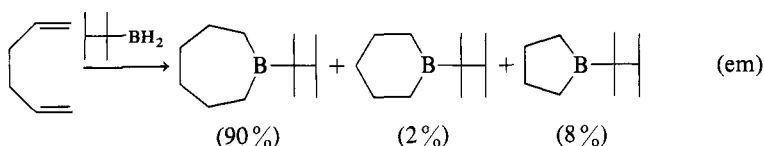
Borane-triethylamine complex proceeds similarly as a hydroborating agent. Low concentration of borane in the mixture provided by slow thermal dissociation of the complex is advantageous in these hydroborations facilitating the formation of cyclic products^{298,300}.

The difunctionality of monoalkyl- and monoarylboranes suits them well for cyclic hydroboration of dienes. The B-alkyl- and B-arylboracycloalkanes can be formed in excellent yields^{301,302}:

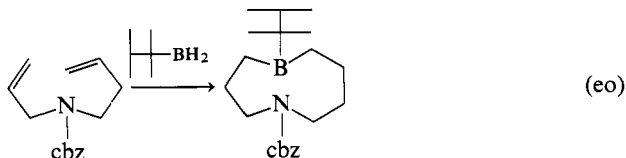


where R = H, Me.

Among these reagents, thexylborane is particularly useful in hydroborating dienes in a highly cyclic manner to give B-thexylboracycloalkanes^{294,303}. Five- to seven-membered rings are favored over six-membered and larger rings:

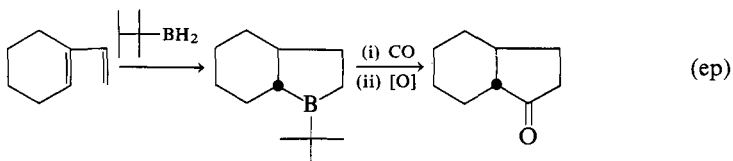


where R = Me and M = Si, Ge and Sn. Formation of the nine-membered ring in the key step of the synthesis of δ -coniceine is facilitated by coordination of thexylborane with the N atom³⁰⁵:

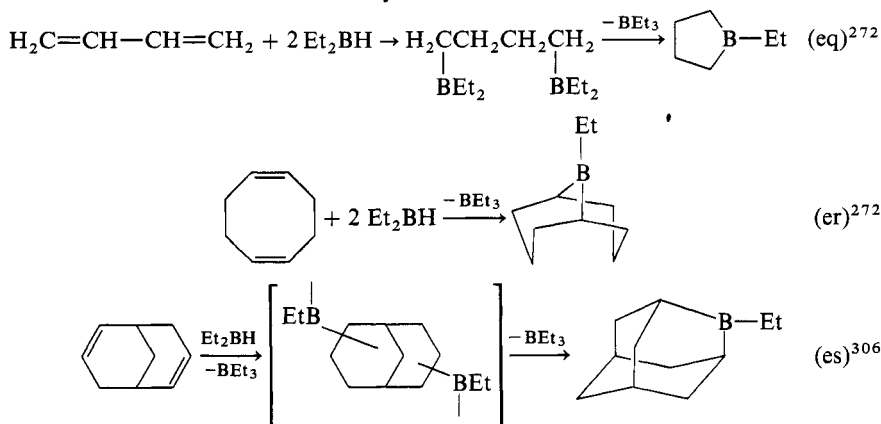


where Cbz is carbobenzyloxy.

Trans-fused bicyclic organoboranes prepared by this method serve as intermediates in a convenient annulation reaction²⁹⁴:



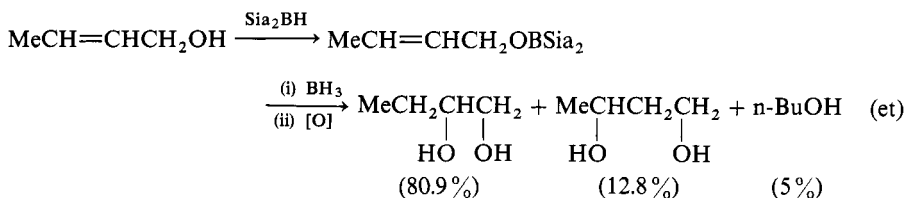
The hydroboration of dienes with lower R_2BH followed by disproportionation is also a convenient route to boraheterocycles:



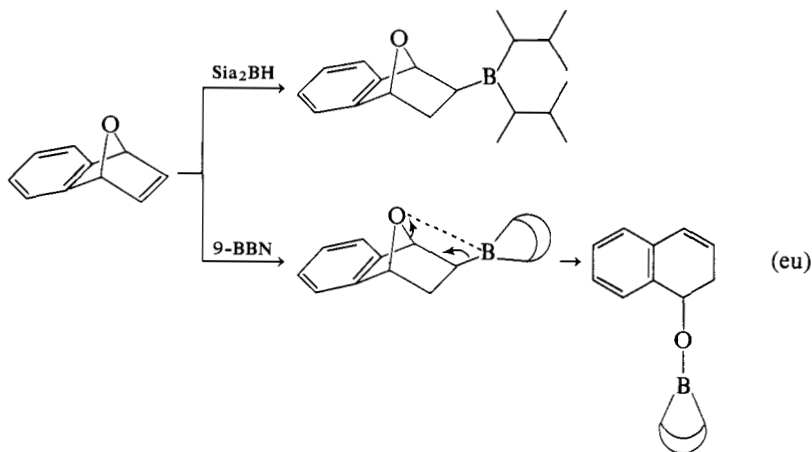
Several cyclic dialkylboranes, e.g., borinane, 3,5-dimethylborinane or 3,6-dimethylborepane, are useful hydroborating agents for the synthesis of the corresponding B-alkyl derivatives¹⁴.

Dihydroboration of dienes and alkynes leads to organoboranes having two boron atoms in the molecule [see Eq. (da), (dm), (dt) and (eh)]. Geminal dibora-derivatives are usually formed from terminal alkynes, whereas internal triple bonds give both vicinal and geminal products^{10,87,99,100,307-311}. The direction of the reaction varies, however, depending on the structure of alkyne and the hydroborating agent.

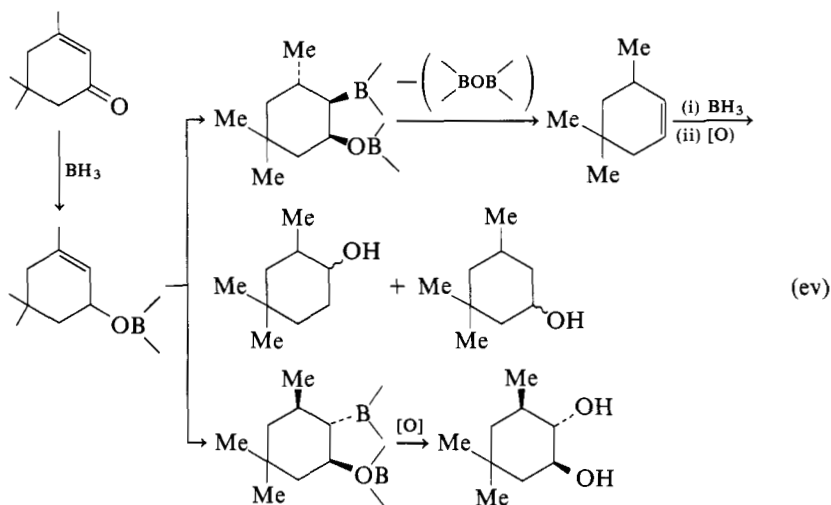
Functionalized alkenes and alkynes can be hydroborated^{5,26}. Directive effects are discussed in §5.3.2.5.1(i). As follows from Table 2, hydroboration of vinylic and allylic derivatives leads to the placement of boron in the α , β or γ position to the substituent. The β -substituted organoboranes are prone to uncatalyzed cis elimination and acid- or base-catalyzed trans-elimination^{107,312}. The rate of elimination depends on the substituent at B, the functional group and the base strength. Good leaving groups, such as Cl and tosylate, undergo fast acid- and base-catalyzed elimination, the basicity of THF being usually sufficient. Elimination of the β -chloroorganoboranes can be avoided by carrying out the hydroboration in the less basic Et_2O , hexane or CCl_4 ^{104,313,314}. The acetate and benzoate groups also undergo fast elimination, via a cyclic transition state. Poor leaving groups, such as borate, phenoxy, ethoxy and alkylthio, undergo slower elimination¹⁰⁷. Consequently, β -substituted organoboranes are obtained, although care must be taken to avoid elimination. Thus, the hydroboration of aliphatic allylic alcohols with borane results in elimination of the intermediate β -substituted organoborane. However, protection of the hydroxyl group as a diisamylborinate, thexylboronate or tetrahydropyranyl ether avoids elimination¹⁰⁶:



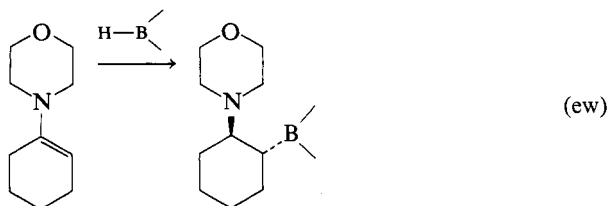
Organoboranes produced by hydroboration of 1,4-epoxy-1,4-dihydronaphthalene with hindered hydroborating agents, e.g., Sia_2BH or dicyclohexylborane, are stable under the reaction conditions, whereas those obtained with $\text{H}_3\text{B}\cdot\text{SMe}_2$ or 9-BBN undergo facile elimination³¹⁵. The boron atom in products derived from the first two reagents is surrounded by bulky substituents, rendering coordination of the 7-oxa substituent to boron difficult. Such coordination to exposed boron must be readily achieved in products derived from $\text{H}_3\text{B}\cdot\text{SMe}_2$ and 9-BBN. Consequently, facile elimination is observed, e.g.:



cis- β -Substituted organoboranes formed in small amounts in the hydroboration of conjugated cyclohexenones and allylic cyclohexanols undergo rapid cis elimination, whereas the trans isomers are stable under the reaction conditions and can be oxidized to the corresponding trans-1,2-diols¹³⁷⁻¹⁴⁰:



Similarly, stable trans- β -aminoorganoboranes can be obtained by the hydroboration of enamines, e.g.^{5,8,11,91-93}:

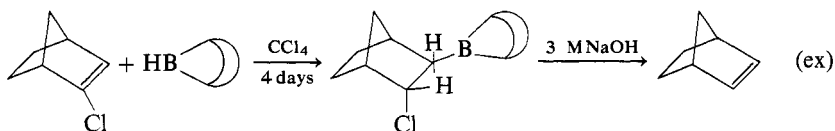


Other unsaturated amines also undergo regio- and stereoselective hydroboration³¹⁶⁻³¹⁹.

The hydroboration of alkylvinyl ethers in hexane provides tris(β -alkoxyethyl)boranes in high yields³¹⁴. Controlled hydroboration conditions and rigorous exclusion of BF_3 are necessary for the efficient synthesis of β -alkoxyorganoboranes from enol ethers³²⁰.

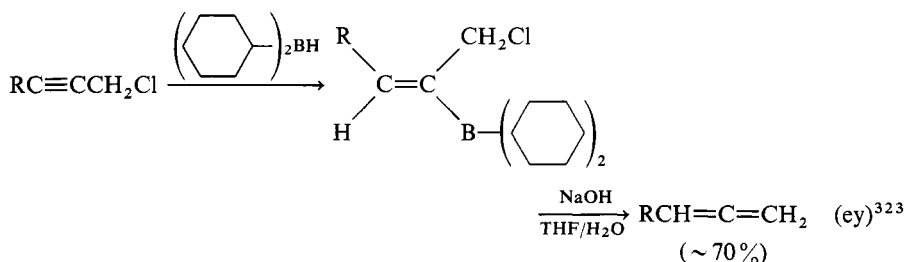
Trimethylsilylenol ethers derived from cyclic ketones are also transformed into the corresponding organoboranes by B_2H_6 ^{321,322}.

Although B_2H_6 is an excellent hydroborating agent, reaction with vinylic and allylic derivatives often leads to mixtures of isomeric organoboranes. Moreover, B_2H_6 reduces many functional groups (see Table 1). The competitive reduction of functional groups is minimized and the regioselectivity is increased by the use of R_2BH , such as diisamylborane^{89,90,106} or 9-BBN¹⁰⁴. The latter reagent is more convenient owing to its higher thermal stability. Selected examples of the synthesis of functionalized B-alkyl-9-BBN derivatives are given in Eqs. (f)–(h). Halogen and alkoxy groups are inert in the hydroboration of functionalized alkenes with 9-BBN, whereas hydroxy groups liberate H_2 with no further reaction; even slowly reducible groups such as ester and nitrile are tolerated, providing organoboranes containing such substituents¹⁰⁴. The highly reactive carbonyl groups in aldehydes and ketones can be protected as the acetals or ketals. Alkenes containing remote functional groups, e.g., $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_n\text{X}$ ($n = 3, 9$; $\text{X} = \text{OH}, \text{COOEt}, \text{OAc}$) are hydroborated with regioselectivity ($\geq 98\%$ terminal placement of boron) producing the corresponding stable B-substituted 9-BBN derivatives. Similarly, allylic and β -methylallyl derivatives are hydroborated so as to place boron on the terminal carbon ($\geq 97\%$ and 99% , respectively)¹⁰⁴. The hydroboration of crotyl derivatives attaches boron predominantly at the 2-position, followed by elimination-rehydroboration. For crotyl alcohol, e.g., elimination can be avoided by protection of the hydroxyl group as *t*-butyl or tetrahydropyranyl ether. The β -substituted organoboranes derived from cyclic vinylic and allylic derivatives are stable under neutral conditions but undergo facile elimination in the presence of base¹⁰⁴:



Several 1-halogeno-1-alkynes and propargylic halides are transformed into the corresponding halogenovinylboranes by hydroboration with R_2BH . These organoboranes are

valuable synthetic intermediates as, e.g. in Eq. (i)¹⁰⁵ and:



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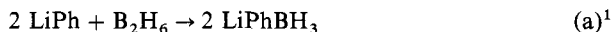
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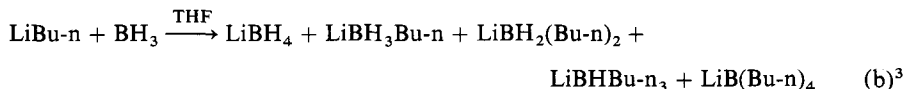
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5.3.2.5.2. by Addition to Polar Organometallics to Form Organoborates.

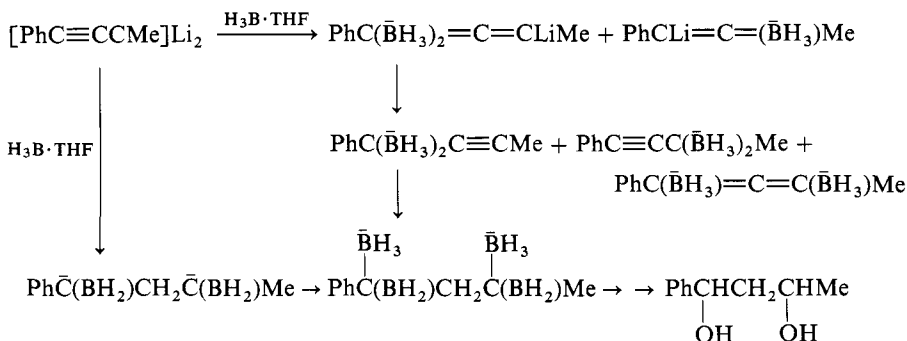
Compared to boron halides and alkoxides, boron hydrides are used less frequently for the formation of B—C bonds in the reaction with polar organometallics. Diborane reacts with these organoboranes or reagents to give the corresponding organoboranes or organoborates. Thus, PhLi reacts with B₂H₆ to yield Li phenylborohydride:



1-Methyldiborane(6) is obtained from CH₃Li with diborane(6)². However, the reaction of n-BuLi with H₃B·THF provides a mixture of all possible borates even at low T:



This difficulty can be partially circumvented using H₃B·SMe₂ at low T⁴. Alternatively, monoalkylborohydrides and dialkylborohydrides are produced by treatment of alkali-

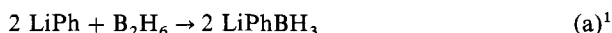


Scheme 1

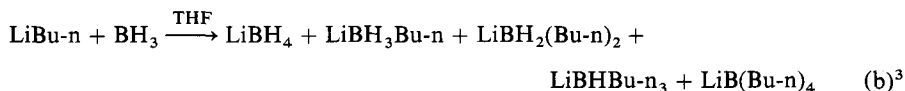
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5.3.2.5.2. by Addition to Polar Organometallics to Form Organoborates.

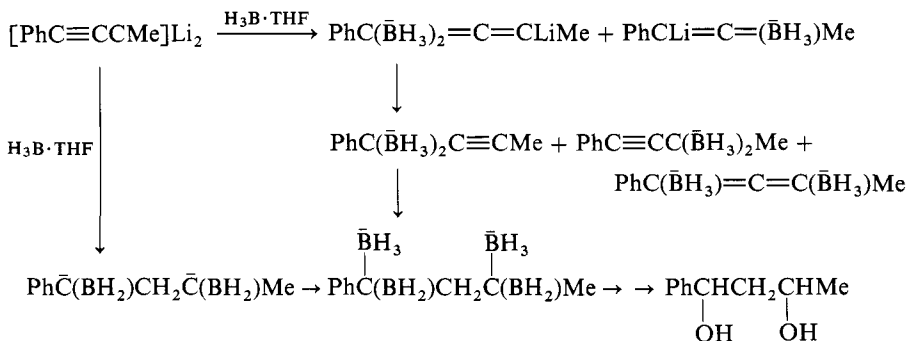
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1-Methyldiborane(6) is obtained from CH₃Li with diborane(6)². However, the reaction of n-BuLi with H₃B·THF provides a mixture of all possible borates even at low T:



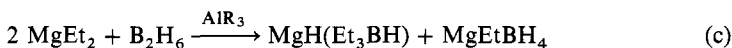
This difficulty can be partially circumvented using H₃B·SMe₂ at low T⁴. Alternatively, monoalkylborohydrides and dialkylborohydrides are produced by treatment of alkali-



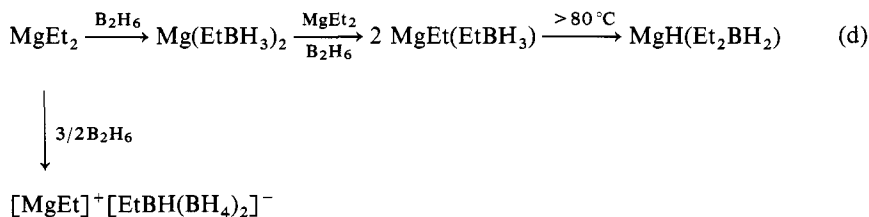
Scheme 1

metal hydrides with mono- and dialkylboranes⁵⁻⁷ or boronic and borinic esters⁸, respectively. These borohydrides are used for selective reductions^{9,10} and storage of mono- and dialkylboranes.

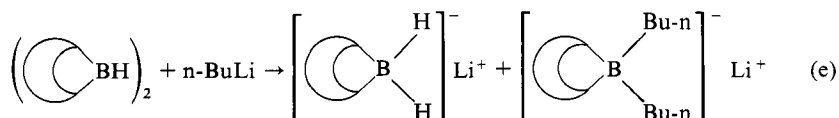
Diethylmagnesium reacts with B₂H₆ in the presence of catalytic amounts of R₃Al to give MgEt borohydrides¹¹:



In the absence of R₃Al, other Mg ethylborohydrides can also be obtained depending on the stoichiometry^{12,13}:

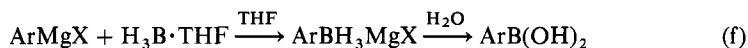


The reaction of MeLi or PhLi with 9-borabicyclo[3.3.1]nonane (9-BBN) and methyl- or n-BuLi with diisopinocampheylborane (IpcBH₂) gives Li organoborates originally believed to be the corresponding simple addition compounds¹⁴⁻¹⁶, [Li(R₂R'BH)]. However, treatment of R₂BH [9-BBN, bis(3-methyl-2-butyl-borane (Sia₂BH), dicyclohexylborane, etc.] with alkyl- or aryllithiums (MeLi, n-BuLi, PhLi, etc.) produces a mixture of two organoborates¹⁷:



The 9-BBN undergoes partial transmetalation with alkyltrimethylstannanes to give B-alkynyl-9-BBN inter alia¹⁸.

Aryl- and alkylorganometallic derivatives of Li¹⁹, Na¹⁹, K¹⁹, Ca¹⁹, Mg²⁰, Hg²¹, Th²², Sn²³, Pb²⁴, Cu²⁵ and Cd^{25,26} react with diborane, transferring one or more organic groups to boron. Hydrolysis or oxidation of the intermediate organoborates gives boronic and borinic acids or phenols, respectively. In this way arylboronic acids are prepared in high yield from arylmagnesium halides and H₃B·THF²⁷:

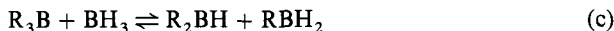


Several equilibria are involved in this reaction, as shown by ¹¹B NMR. The metalation-hydroboration of acetylides leads to 1,3-diols. A possible sequence of transformations for the reaction of H₃B·THF with propargylic lithium derivative is²⁸.

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5.3.2.5.3. by Redistribution of Organoboron Hydrides.

Redistribution of organoboron hydrides and the closely related exchange between B_2H_6 and trialkyl- and triarylboranes is used for the synthesis of alkyl- and arylidiboranes¹⁻⁴. These are equilibrium processes leading to mixtures of products:



Formation of these B_2H_6 dimer derivatives is possible: $RHBH_2BH_2$, $R_2BH_2BH_2$, $RHBH_2BHR$, R_2BH_2BHR and $R_2BH_2BR_2$. The dimer-monomer equilibria accounting for disproportionation are shifted to the dimer side, both in free compounds and in ether⁵⁻⁹. Only hindered alkylboranes, e.g., bis(2,3-dimethyl-2-butyl)borane (dithexylborane)¹⁰ or bis[1-(trimethylsilyl)-1-propyl]borane¹¹, are monomers.

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5.3. Formation of Bonds

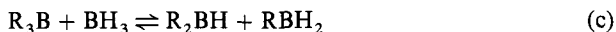
5.3.2. Formation of Carbon—Boron Bonds

5.3.2.5. from Boron Hydrides

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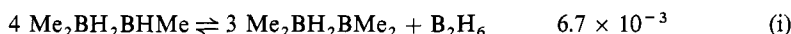
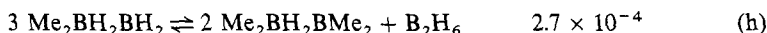
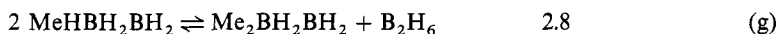
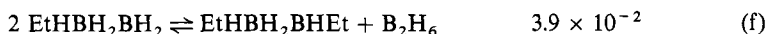
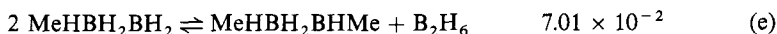
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The formation of mixtures, rendering product isolation difficult, is the major limitation of disproportionation as a method for B—C bond construction. However, when the equilibria are favorable to one compound or the products can be readily

separated, the method is of preparative value. Thus, all possible methyl- and ethyldiboranes, except symmetrical dialkyldiboranes, are obtained from B_2H_6 and Me_3B and Et_3B , respectively¹²⁻¹⁹:

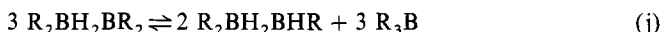


where $R = Me, Et$. Symmetrical dimethyl- and diethyldiboranes are synthesized by disproportionation of the corresponding unstable monoalkyldiboranes^{15,17}. Approximate equilibrium constants for these and other reactions are^{2,15,20}:



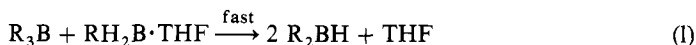
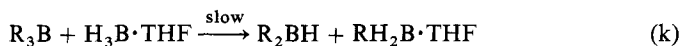
The reaction of B_2H_6 with 1,2-diethyldiborane (Eq. f) reaches equilibrium rapidly and is utilized for purification of 1,1-diethyldiborane¹⁵. When a mixture of 1,1- and 1,2-diethyldiboranes is treated with B_2H_6 , the 1,2-isomer is transformed into monoethyldiborane, whereas the 1,1-isomer remains unchanged.

Lower $R_4B_2H_2$ are in equilibrium with trialkyldiboranes^{7,9,18}:



At 30°C by ^{11}B NMR the equilibrium ($R = Et, n-Pr, n-Bu, i-Bu$) is composed of tetraethyldiborane (~90%), 1,1,2-triethyldiborane (~5%) and traces of BEt_3 . At 70°C, 1,1,2-trialkyldiboranes become the principal products in the equilibrium mixture⁷, but 1,1- and 1,2-dialkyldiboranes and R_3B are also present. The R_3B increases with increasing size of the alkyl group, e.g., at 110°C, BEt_3 (5-7%), $BPr-n_3$ (~10%), $BBu-i_3$ (~15%), $BBu-n_3$ (~20%).

In ethers alkyldiboranes also exist in equilibrium mixtures. In the reaction⁹ of $H_3B \cdot THF$ with lower R_3B , 1,1-dialkyldiborane is the first product observed by variable-T ^{11}B NMR after the reagents are mixed:



The consecutive steps depend on the $R_3B:BH_3$ ratio and on the R group. Similar equilibria are observed for $H_3B \cdot SMe_2$ ²¹ with lower R_3B and for other alkyldiboranes^{22,23}; e.g., the exchange of tri-exo-norbornylborane and tricyclopentylborane with $BH_3 \cdot THF$ gives a distribution of products²³ (see Table 1).

TABLE 1. PRODUCTS FROM TRI-EXO-NORBORNYL- AND TRICYCLOPENTYLBORANE

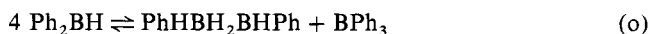
BR ₃ :BH ₃ molar ratio	R	BH ₃ (%)	RBH ₂ (%)	R ₂ BH (%)	BR ₃ (%)
2:1	cyclopentyl	3-4	25-30	52-55	12-15
	norbornyl	4-2	26-27	54-60	11-17
1:2	cyclopentyl	20-24	48-52	27-30	0-2
	norbornyl	14-17	72-75	13-12	0-2

Disproportionation of phenyldiboranes reveals differences compared to alkyl diboranes. Thus, in contrast to Me₃B and Et₃B, exchange of Ph₃B with B₂H₆, both in the vapor and in ether, yields 1,2-diphenyldiborane^{24,25}:

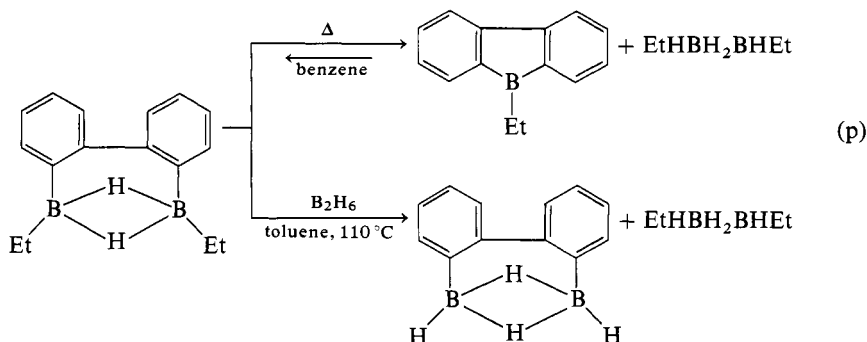


The product is stable at RT and can be isolated by removing the solvent²⁵. Equilibrium (n) must also exist in the absence of solvent, since pure 1,2-diphenyldiborane does not sublime, even in vacuum, whereas it does²⁴ in the presence of B₂H₆.

Diphenylborane generated by reduction of diphenylborinic acid ester redistributes rapidly to the mixture of Ph₃B and 1,2-diphenyldiborane²⁵:



For isolation, it must be stabilized by complexation with amines²⁶. Disproportionation of organoboron hydrides is used in the synthesis of boraheterocycles via hydroboration, as well as in the synthesis of arylboraheterocycles^{3,27}:



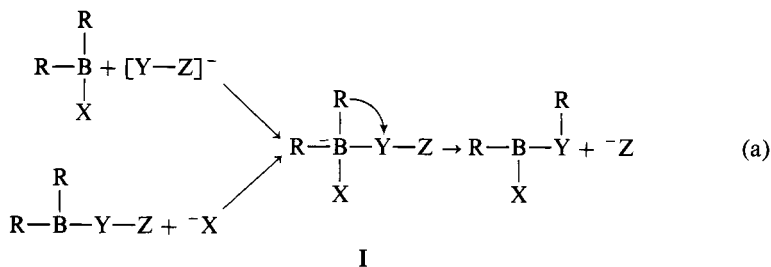
(H. C. BROWN, M. ZAJDLIEWICZ)

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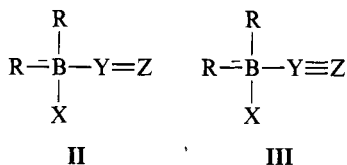
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5.3.2.6. from Organoboranes

Organoboranes can be prepared from other organoboranes by organoborane-interconverting reactions. Organoboranes can form C—C and C-hetero atom bonds by conversion of one organoborane into another via 1,2 migration of an organoborate intermediate:¹



The double- and triple-bonded analogues of the borate (I), i.e., II and III, can also participate in related reactions.



5.3. Formation of Bonds

91

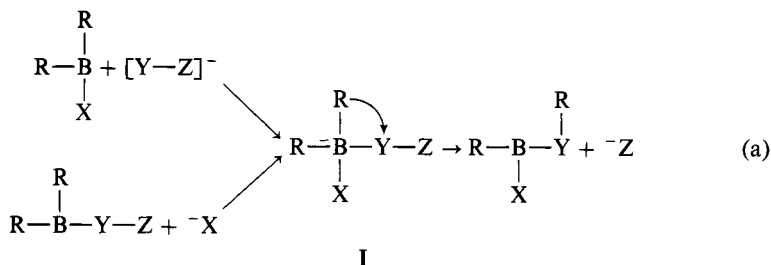
5.3.2. Formation of Carbon—Boron Bonds

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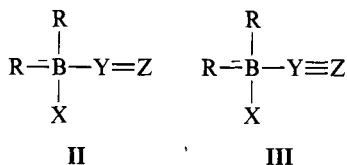
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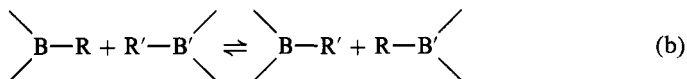
The double- and triple-bonded analogues of the borate (I), i.e., **II** and **III**, can also participate in related reactions.



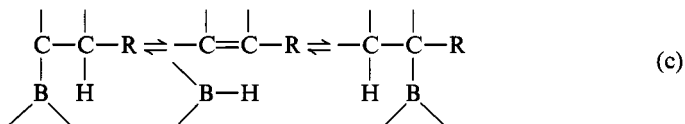
This discussion, however, is restricted to those organoborane interconversions that either occur thermally or involve addition of the B—C bond to olefinic or acetylenic linkages.

Organoboranes can undergo three types of thermal reactions:

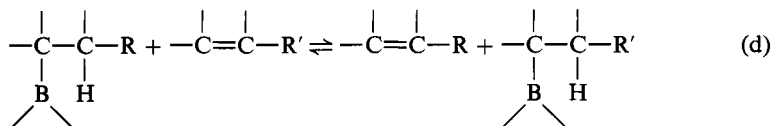
(1) redistribution^{2,13}:



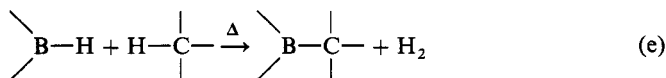
(2) isomerization⁴:



and displacement:



and (3) substitution^{2,4}:



Redistribution of organoboranes can proceed even at or below RT. On the other hand, isomerization and displacement usually require $\geq 50^\circ\text{C}$, typically $150\text{--}160^\circ\text{C}$. Substitution (Eq. e) proceeds at reasonable rates only at $>200^\circ\text{C}$.

(E. I. NEGISHI)

- For reviews, see (a) H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972; (b) H. C. Brown, *Organic Synthesis via Boranes*, Wiley-Interscience, New York, 1975; (c) G. M. L. Cragg, *Organoboranes in Organic Synthesis*, Marcel Dekker, New York, 1973; (d) A. Pelter, K. Smith, in *Comprehensive Organic Chemistry*, D. H. R. Barton, W. D. Ollis, eds., Vol. 3, D. N. Jones, Pergamon, Oxford, 1979; (e) E. Negishi, *Organometallics in Organic Synthesis*, ed., Vol. 1, Wiley-Interscience, New York, 1980; (f) E. Negishi, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon, Oxford, 1982, Chs. 45.6–45.11; (g) E. Negishi, M. J. Idacavage, *Org. React.*, 33, 1 (1985).
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- H. C. Brown, E. Negishi, *Tetrahedron*, 33, 2331 (1977).

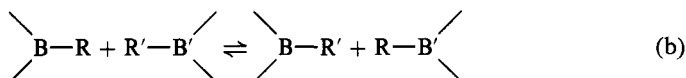
5.3.2.6.1. by Redistribution.

Redistribution is the most facile thermal reaction that organoboranes undergo. Because it can occur at $\leq 0^\circ\text{C}$, hydroboration is usually accompanied by this reaction. It

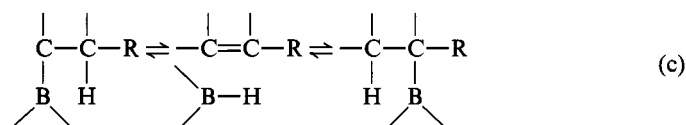
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Organoboranes can undergo three types of thermal reactions:

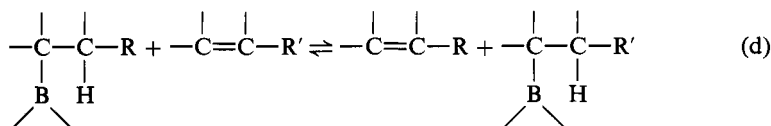
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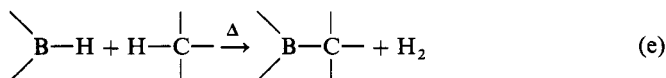
(2) isomerization⁴:



and displacement:



and (3) substitution^{2,4}:



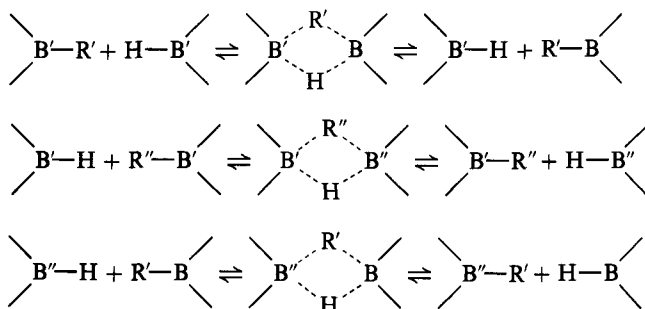
Redistribution of organoboranes can proceed even at or below RT. On the other hand, isomerization and displacement usually require $\geq 50^\circ\text{C}$, typically $150\text{--}160^\circ\text{C}$. Substitution (Eq. e) proceeds at reasonable rates only at $>200^\circ\text{C}$.

(E. I. NEGISHI)

1. For reviews, see (a) H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972; (b) H. C. Brown, *Organic Synthesis via Boranes*, Wiley-Interscience, New York, 1975; (c) G. M. L. Cragg, *Organoboranes in Organic Synthesis*, Marcel Dekker, New York, 1973; (d) A. Pelter, K. Smith, in *Comprehensive Organic Chemistry*, D. H. R. Barton, W. D. Ollis, eds., Vol. 3, D. N. Jones, Pergamon, Oxford, 1979; (e) E. Negishi, *Organometallics in Organic Synthesis*, ed., Vol. 1, Wiley-Interscience, New York, 1980; (f) E. Negishi, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon, Oxford, 1982, Chs. 45.6–45.11; (g) E. Negishi, M. J. Idacavage, *Org. React.*, **33**, 1 (1985).
2. R. Köster, *Adv. Organomet. Chem.*, **2**, 257 (1964).
3. R. Köster, *Prog. Boron Chem.*, **1**, 289 (1964).
4. H. C. Brown, E. Negishi, *Tetrahedron*, **33**, 2331 (1977).

5.3.2.6.1. by Redistribution.

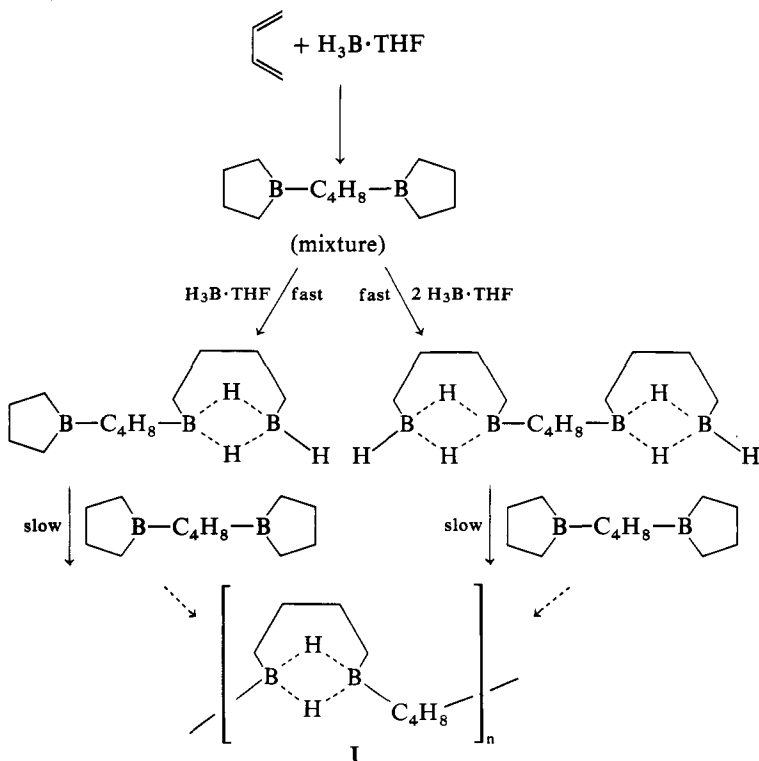
Redistribution is the most facile thermal reaction that organoboranes undergo. Because it can occur at $\leq 0^\circ\text{C}$, hydroboration is usually accompanied by this reaction. It



Scheme 1

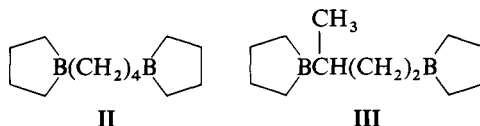
is catalyzed by boron hydrides by the mechanism shown in Scheme 1, involving three-center, two-electron bonds. In accord with this disproportionation proceeds with retention of configuration of the organic groups.

The significance of disproportionation is shown by the 1:1 reaction of 1,3-butadiene with $\text{H}_3\text{B} \cdot \text{THF}$ (THF = tetrahydrofuran)¹, which produces a polymer best represented by I. The results can be rationalized by a mechanism involving hydroboration followed by a series of disproportionations (Scheme 2).

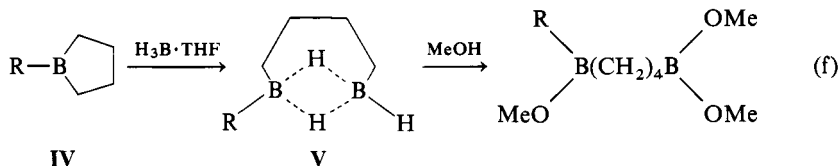


Scheme 2

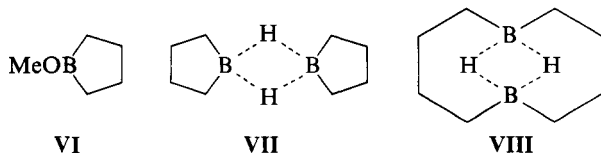
Several lines of evidence support Scheme 2. First, if the ratio of 1,3-butadiene and $\text{H}_3\text{B}\cdot\text{THF}$ is 3:2, a mixture of dumbbell-shaped products, **II** and **III**, is obtained in excellent yield².



Addition of half the original amount of $\text{H}_3\text{B}\cdot\text{THF}$ to this mixture produces **I**¹. Second, treatment of B-alkylborolanes **IV** with 1 equiv. $\text{H}_3\text{B}\cdot\text{THF}$ rapidly and quantitatively produces **V** by disproportionation³:

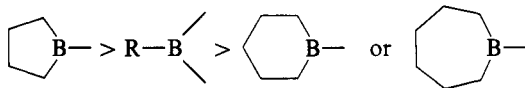


Third, the 1:1 product reacts with CH_3OH or an alkene but does not directly produce any volatile product, such as B-methoxyborolane, **VI** or **IV**, although **IV** or **VI** is formed in good yield on heating¹. This rules out **VII** as the structure of the 1:1 product.

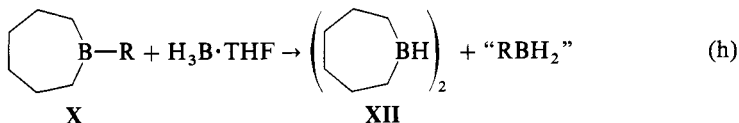
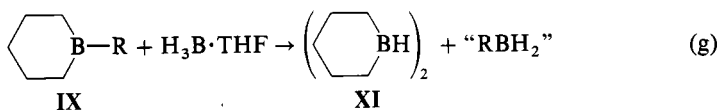


Fourth, the other dimeric product, **VIII** is formed in 70% yield³ when the 1:1 product is heated and distilled. However, **VIII** is inert to CH_3OH or alkenes at RT and is, therefore, a completely different species than the initial 1:1 product. Fifth, **VII**, prepared by an indirect method, is highly reactive⁴. These results are thus consistent with Scheme 2 and the assignment of **I**, **VII**, and **VIII** to the three 1:1 products that are characterized.

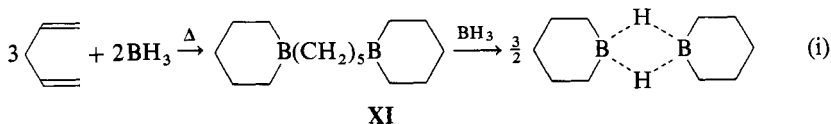
The order of reactivity of B—C bonds toward $\text{H}_3\text{B}\cdot\text{THF}$ is:



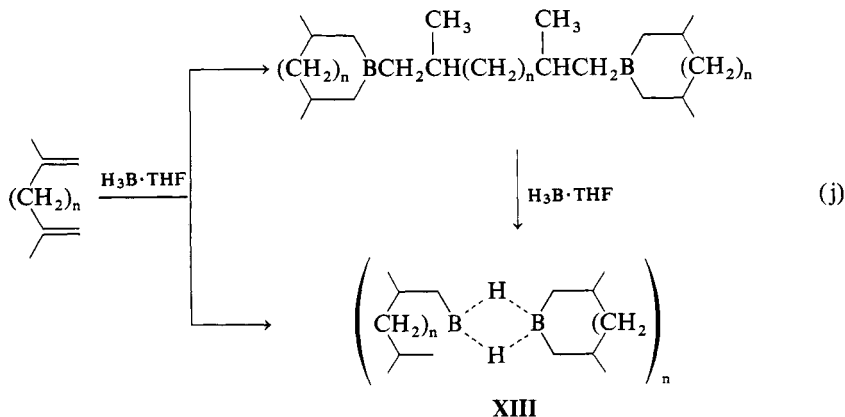
Thus, treatment of a B-alkylborinane (**IX**) or a B-alkylborepane (**X**) with 1 equiv $\text{H}_3\text{B}\cdot\text{THF}$ produces borinane (**XI**) or borepane (**XII**), respectively^{5,6}.



This property can be exploited in the preparation of borinane (XI) free from the other compounds⁷:



Certain dimethyl-substituted borinanes and borepanes, e.g., XIII, can be produced directly^{8,9}. Even so, the reaction involves disproportionation of the dumbbell-shaped product initially formed:



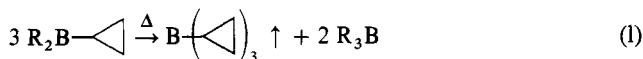
where $n = 1$ or 2 .

Redistribution can also be used to produce B-alkylboracyclanes^{10,11}:



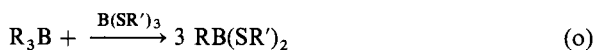
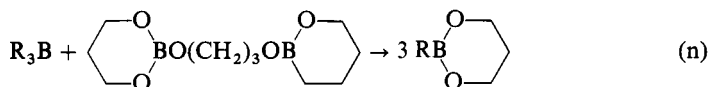
although it is better to prepare the parent boracyclanes and convert them into B-alkylboracyclanes by hydroboration or other methods.

In redistributions of R_3B incapable of forming boracyclanes, statistical mixtures of products can result. If the equilibrium can be shifted by selective removal of one or more components, however, the reaction may still be of synthetic use; e.g., tricyclopropylborane can be synthesized by disproportionation-distillation of a dialkylcyclopropyl borane¹².

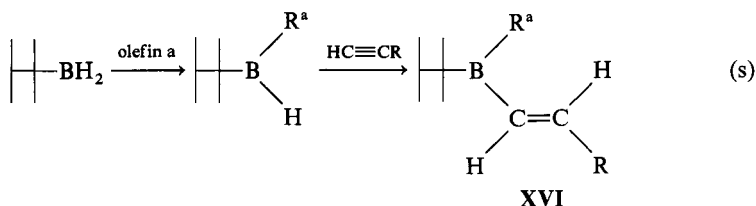
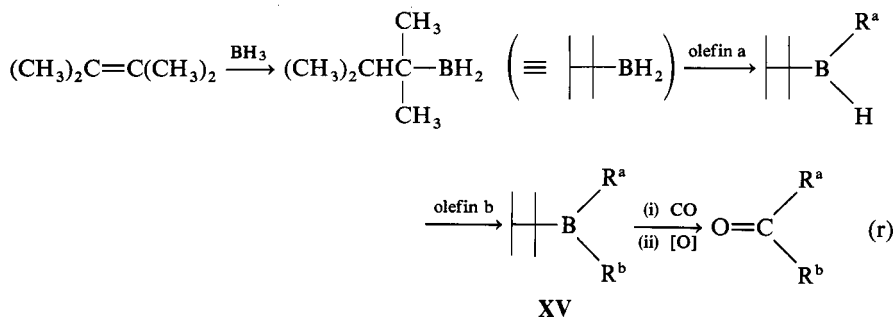
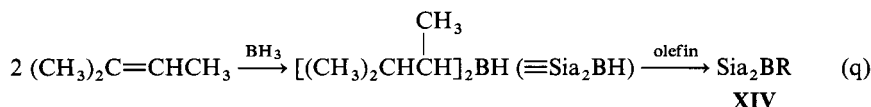


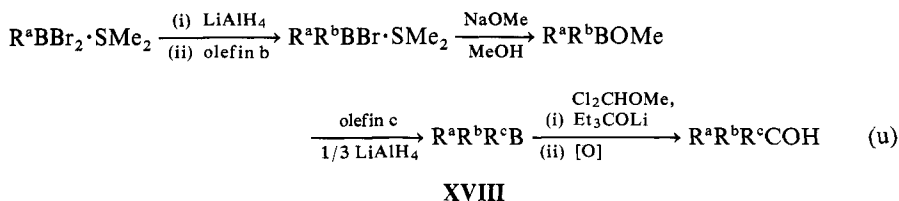
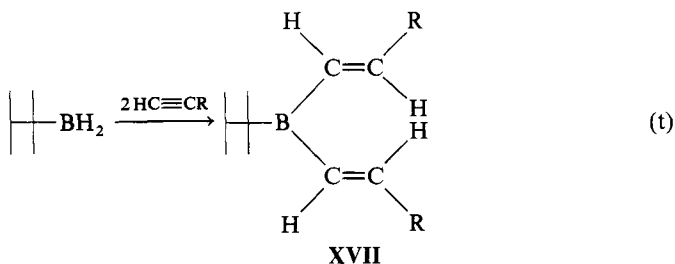
If redistribution proceeds through the formation of three-center, two-electron bonds (Scheme 1), alkenyl, aryl, alkynyl, allyl, benzyl and propargyl groups should participate more readily than the alkyl group, but this point is not established. Catalysis by boron hydrides is not applicable where alkenyl or alkynyl groups are present, because the boron hydrides are consumed through hydroboration.

Redistribution is not restricted to exchanges between two carbon groups or to those between one carbon group and a hydrogen. Heteroatoms, such as those containing halogens¹³, oxygen¹⁴, sulfur¹⁵ and nitrogen¹⁶ participate:



Disproportionation of organoboranes at or below RT is facile only in the presence of a boron hydride or other catalytic species, e.g., organoalanes. In their absence, organoboranes do not disproportionate readily at RT. Thus, mixed $R^aR^bR^cB$ and $R^aR^bR^cB$ organoboranes are used as intermediates for organic synthesis¹⁷. The mixed acyclic organoboranes include diisoamylalkylboranes¹⁸ (XIV), thexyldialkylboranes^{19–21} (XV), thexylalkenylalkylboranes^{19–21} (XVI), thexyldialkenylboranes^{19–21} (XVII) and totally mixed trialkylboranes²² (XVIII), where thexyl is 2,3-dimethyl-2-butyl and Sia_2BH is diisoamylborane:





(E. I. NEGISHI)

1. H. C. Brown, E. Negishi, P. L. Burke, *J. Am. Chem. Soc.*, **93**, 3400 (1971).
2. H. C. Brown, E. Negishi, S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 2460 (1970).
3. E. Breuer, H. C. Brown, *J. Am. Chem. Soc.*, **91**, 4164 (1969), E. Breuer, H. C. Brown, *Israel J. Chem.*, **2**, 238 (1964).
4. H. C. Brown, E. Negishi, *J. Am. Chem. Soc.*, **93**, 6682 (1971).
5. E. Negishi, P. L. Burke, H. C. Brown, *J. Am. Chem. Soc.*, **94**, 7431 (1972).
6. L. Burke, E. Negishi, H. C. Brown, *J. Am. Chem. Soc.*, **95**, 3654 (1973).
7. H. C. Brown, E. Negishi, *J. Organomet. Chem.*, **26**, C67 (1971).
8. H. C. Brown, E. Negishi, *J. Organomet. Chem.*, **28**, C1 (1971).
9. E. Negishi, H. C. Brown, *J. Am. Chem. Soc.*, **95**, 6757 (1973).
10. R. Köster, *Adv. Organomet. Chem.*, **2**, 257 (1964).
11. R. Köster, *Prog. Boron Chem.*, **1**, 289 (1964).
12. P. Binger, R. Köster, *Angew. Chem., Int. Ed. Engl.*, **1**, 58 (1962).
13. H. C. Brown, A. B. Levy, *J. Organomet. Chem.*, **44**, 233 (1972).
14. H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 6983 (1970).
15. B. M. Mikhailov, L. S. Vasilev, *Dokl. Akad. Nauk. SSSR*, **139**, 385 (1961).
16. G. E. Coates, *J. Chem. Soc.*, 3481 (1950).
17. For reviews see ref. 1 in §5.3.2.6.
18. H. C. Brown, G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960).
19. E. Negishi, H. C. Brown, *Synthesis*, **77** (1974).
20. S. U. Kulkarni, H. D. Lee, H. C. Brown, *J. Org. Chem.*, **45**, 4542 (1980).
21. G. Zweifel, N. R. Pearson, *J. Am. Chem. Soc.*, **102**, 5919 (1980).
22. S. U. Kulkarni, D. Basavaiah, M. Zaidlewicz, H. C. Brown, *Organomet.*, **1**, 212 (1982).

5.3.2.6.2. by Isomerization and Displacement.

Organoboranes can undergo isomerization that involves transfer of a boron atom from one carbon to another within the same organic group, without being accompanied by carbon skeletal rearrangement. In redistribution the boron-bearing carbons remain the same.

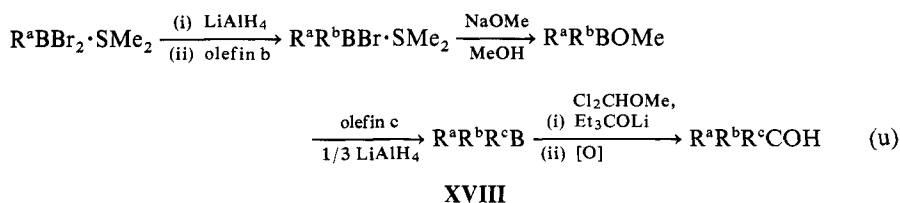
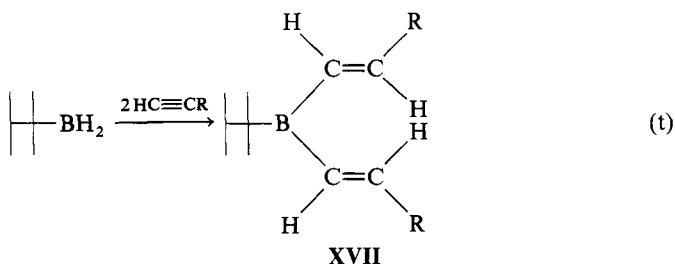
Typical R_3B 's isomerize at useful rates at ca. 150°C , providing equilibrium mixtures of products. Usually, the thermodynamically most stable alkylboranes are those in which

5.3. Formation of Bonds

97

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.6. from Organoboranes



(E. I. NEGISHI)

1. H. C. Brown, E. Negishi, P. L. Burke, *J. Am. Chem. Soc.*, **93**, 3400 (1971).
2. H. C. Brown, E. Negishi, S. K. Gupta, *J. Am. Chem. Soc.*, **92**, 2460 (1970).
3. E. Breuer, H. C. Brown, *J. Am. Chem. Soc.*, **91**, 4164 (1969), E. Breuer, H. C. Brown, *Israel J. Chem.*, **2**, 238 (1964).
4. H. C. Brown, E. Negishi, *J. Am. Chem. Soc.*, **93**, 6682 (1971).
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6. L. Burke, E. Negishi, H. C. Brown, *J. Am. Chem. Soc.*, **95**, 3654 (1973).
7. H. C. Brown, E. Negishi, *J. Organomet. Chem.*, **26**, C67 (1971).
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18. H. C. Brown, G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3222 (1960).
19. E. Negishi, H. C. Brown, *Synthesis*, 77 (1974).
20. S. U. Kulkarni, H. D. Lee, H. C. Brown, *J. Org. Chem.*, **45**, 4542 (1980).
21. G. Zweifel, N. R. Pearson, *J. Am. Chem. Soc.*, **102**, 5919 (1980).
22. S. U. Kulkarni, D. Basavaiah, M. Zaidlewicz, H. C. Brown, *Organomet.*, **1**, 212 (1982).

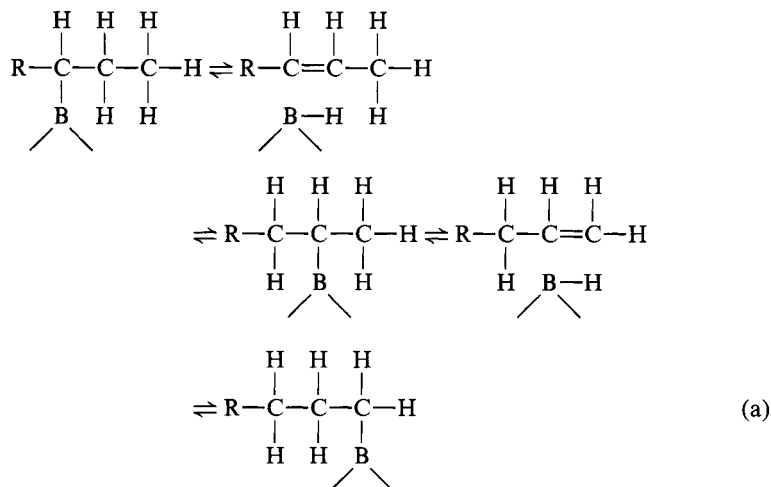
5.3.2.6.2. by Isomerization and Displacement.

Organoboranes can undergo isomerization that involves transfer of a boron atom from one carbon to another within the same organic group, without being accompanied by carbon skeletal rearrangement. In redistribution the boron-bearing carbons remain the same.

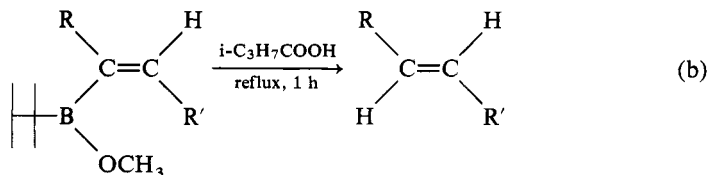
Typical R_3B 's isomerize at useful rates at ca. 150°C, providing equilibrium mixtures of products. Usually, the thermodynamically most stable alkylboranes are those in which

the boron atoms are placed at the least hindered positions of the alkyl groups, e.g., the terminal carbon atoms. However, other factors may place boron at nonterminal positions, e.g., the stability of boracyclanes is influenced by their ring size (see below), and borons in the equilibrated boracyclanes are often found at nonterminal positions¹.

Isomerization of alkylboranes proceeds via dehydroboration–rehydroboration².



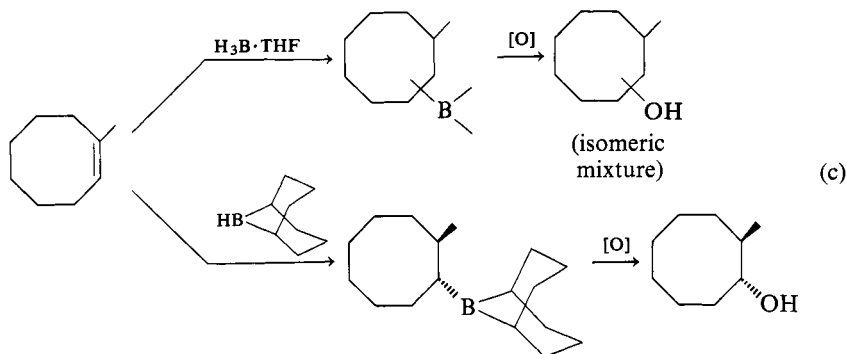
If this mechanism is correct, isomerization may proceed past secondary or tertiary carbons but may not proceed past a quaternary carbon center, and this is the case. This mechanism is also consistent with the lack of isomerization involving migration of borons in aryl- and alkynylboranes. Alkynyl groups cannot participate in dehydroboration, and dehydroboration of arylboranes, which would produce benzyne, requires a high activation energy. In principle, alkenylboranes containing *cis*- β -hydrogens can dehydroborate and induce isomerization. However, there is no evidence for such a reaction. Moreover, alkenylboranes can be protonolyzed at ca. 155°C in isobutyric acid to form stereo- and regiochemically pure alkenes in high yields³, indicating that alkenylboranes are stable to isomerization even at such high T.



Allyl- and propargylboranes undergo different isomerizations (see below), but the benzyl–boron bond is stable to isomerization.

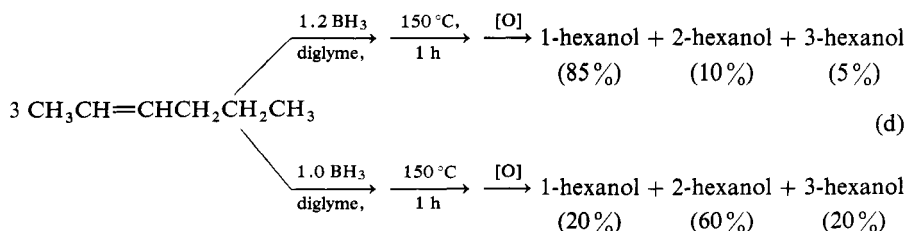
The ease of dehydroboration of alkylboranes decreases in the order: tertiary > secondary > primary. The order of the ease of hydroboration is opposite to this. Both factors contribute to the order of isomerization decreasing tertiary > secondary > primary. Isomerization of sterically hindered or strained alkylboranes may occur even at RT; e.g., oxidation of freshly prepared 2,3-dimethyl-2-butylborane (thexylborane) gives a 99:1 mixture of 2,3-dimethyl-2-butanol and 2,3-dimethyl-1-butanol, whereas oxidation

of an aged sample stored for 16 days at RT in tetrahydrofuran (THF) gives a 91:9 mixture of the two alcohols⁴. Similarly, the hydroboration-oxidation of 1-methylcyclooctene using $\text{H}_3\text{B}\cdot\text{THF}$ does not yield exclusively 2-methylcyclooctanol but gives a mixture of methylcyclooctanols⁵. Use of 9-borabicyclo[3.3.1]nonane (9-BBN), however, circumvents the difficulty and permits the formation of trans-2-methylcyclooctanol in 90% yield⁶:



The reluctance of the 9-BBN moiety to move along the C-skeleton may be a reflection of the smaller steric crowding in the 9-BBN derivative, as compared with the organoborane intermediate in the $\text{H}_3\text{B}\cdot\text{THF}$ reaction.

Isomerization of organoboranes can involve unhindered alkyl groups⁷. Trihexylboranes derived from 2-hexene and the stoichiometric amount of borane isomerizes at 150°C more slowly than when 20% xs boron hydride reagent is present⁷:



where diglyme is diethyleneglycol dimethyl ether. The equilibrium composition and the approximate time required for completion of isomerization at 160°C for representative olefins are summarized in Table 1⁷.

The steric crowding in organic groups that do not participate in isomerization can also exert an effect not only on the rate of isomerization, but also on the product distribution. The relative rates of isomerization of dialkyl-3-hexylboranes in the absence of a hydride reagent at 150°C are summarized in Table 2⁸.

In the thermal isomerization of boracyclanes, the equilibrium positions of the borons are often dictated by their ring size. Given a choice, borinane (boracyclohexane) is formed preferentially. Other factors not encountered in the isomerization of acyclic alkylboranes may affect the isomerization of boracyclanes¹, as discussed below.

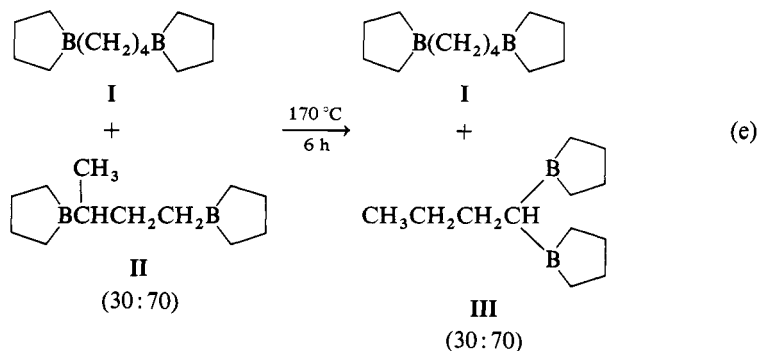
The stoichiometric hydroboration of 1,3-butadiene with borane·THF gives a 30:70 mixture of dumbbell-shaped **I** and **II** as the kinetic products⁹. When the mixture is heated to 140–170°C, a ca. 30:70 mixture of **I** and a new isomer **III**, along with a small amount of

TABLE 1. ISOMERIZATION OF ORGANOBORANES AT 160°C^a

Olefin	Time for completion (h)	Alcohol (%)			
		1-ol	2-ol	3-ol	4-ol
1-Pentene	2	93	5	2	
2-Pentene	2	95	4	1	
2-Methyl-1-butene	4	56	1	trace	43
3-Methyl-1-butene	4	59	1	trace	40
2-Methyl-2-butene	2	57	2	trace	41
3,3-Dimethyl-1-butene	<4	99	1		
2,4,4-Trimethyl-1-pentene	1	99	trace	1	
Styrene	<4	80	20		
Allylbenzene	1 ^b	85	7	8	
1-Phenyl-1-propene	4 ^b	78	9	13	

^a Run in the presence of 20% xs borane.^b Equilibrium mixtures may not be obtained under the conditions used.

II is obtained⁹. The predominant formation of the 1,1-dibora species **III** cannot readily be explained by steric factors:



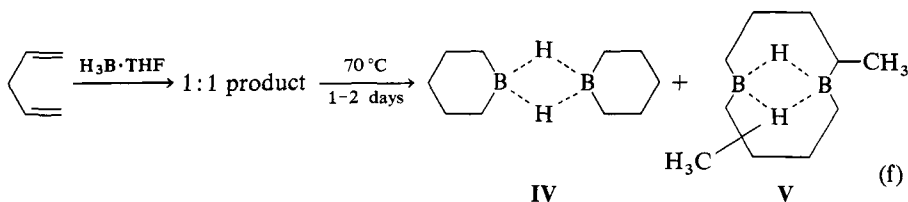
The 1:1 hydroboration of 1,4-pentadiene with $\text{H}_3\text{B}\cdot\text{THF}$ gives, after oxidation, a 45:55 mixture of 1,4- and 1,5-pentanediols. Upon heating this kinetic, 1:1 hydroboration

TABLE 2. ISOMERIZATION OF DIALKYL-3-HEXYLBORANES IN DIGLYME^a AT 150°C

Dialkylboryl	Time for completion (h)	Alcohol (%)		
		1-ol	2-ol	3-ol
9-BBN ^b	264	90	6	4
Di-3-hexylboryl	72	90	6	4
Dicyclohexylboryl	48	97	2	1
Bis(2,5-dimethylcyclohexyl)boryl	0.5	100	0	0

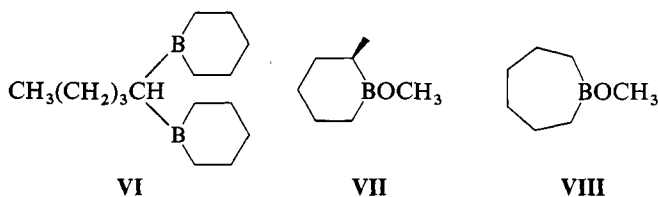
^a Diglyme is diethyleneglycol dimethylether.^b 9-BBN is 9-borabicyclo[3.3.1]nonane.

product for 1–2 days at 70°C, a 45:55 mixture of borinane (IV) and dimethyl-1,6-diboracyclodecane (V) is formed in 90% combined yield¹⁰. The only low mol wt product present in the initial kinetic mixture is borinane (~25%). Thus, when heated, the polymeric initial product is converted into the volatile products IV and V. However, these conversions merely involve disproportionation and little or no isomerization under these conditions:



Thermal treatment at 120–170°C of the 1:1 product derived from 1,4-pentadiene and $\text{H}_3\text{B} \cdot \text{THF}$ follows an unexpected course. As summarized in Table 3¹⁰, the amount of 1,5-pentanediol decreases to ca. 33% on heating. Furthermore, the volatile products IV and V, as well as that of the alcohols, decrease with time. Thus, under these conditions, the product is slowly converted into new species that cannot be oxidized readily, e.g., carboranes.

Thermal isomerization of the 1,4-diborapentane to the 1,5-diborapentane moiety can be achieved by heating the 3:2 hydroboration product to 170°C for several hours. After oxidation, 1,5- and 1,4-pentanediols as well as 1-pentanol are obtained in quantitative combined yield as an 80:10:10 mixture¹⁰. 1-Pentanol is derived from VI:



Alkaline H_2O_2 oxidation of the 3:2 hydroboration product derived from 1,5-hexadiene and $\text{H}_3\text{B} \cdot \text{THF}$ gives 1,6-, 1,5- and 2,5-hexanediols in 73, 19, and 5% yields,

TABLE 3. THERMAL TREATMENT AT 170°C OF THE 1:1 HYDROBORATION PRODUCT DERIVED FROM 1,4-PENTADIENE AND BORANE

Time (h)	GLC ^a yield (%)			GLC ^a yield of oxidation product (%)			
	14 ^b	23	Total	1,5-Diol	1,4-Diol	1-Pentanol	Total
0	25	0	25	46	57	0	103
1	20	51	71	33	37	9	93
3	11	10	22	38	22	28	88
6	5	4	9	33	10	35	79

^a As measured by gas-liquid chromatography (GLC).

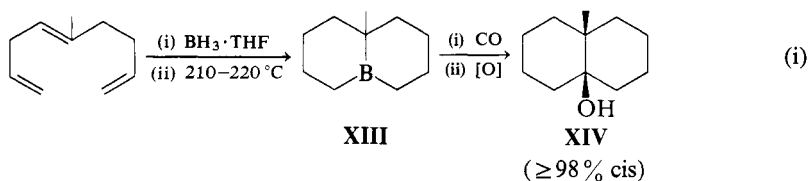
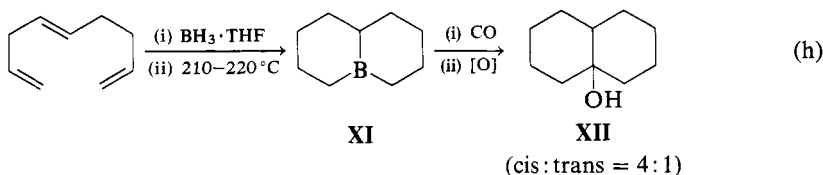
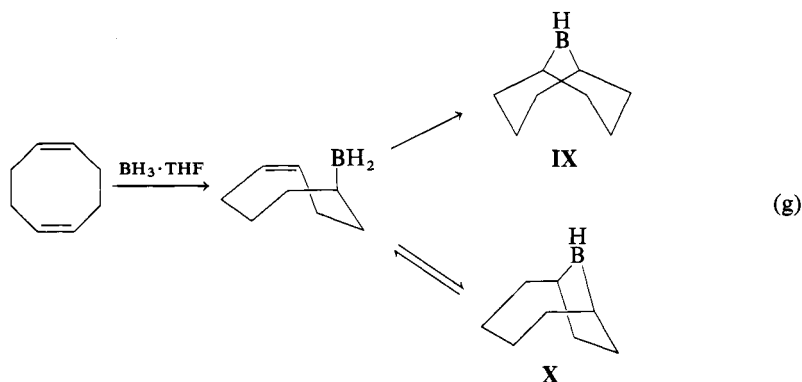
^b As B-methoxyborinane.

respectively¹¹. After heating the 3:2 product for 6 h at 170°C, followed by oxidation, 1,6- and 1,5-hexanediols as well as 1-hexanol are obtained in 27, 62 and 8% yields, respectively¹¹. Treatment of the 3:2 kinetic product with 1 mol equiv of $\text{H}_3\text{B}\cdot\text{THF}$ for 1–2 days at RT, followed by methanolysis, gives **VII** and **VIII** in 20 and 55% yields, respectively¹¹. The same treatment of the 3:2 thermal product (3 h at 170°C) provides the two methanolysis products **VII** and **VIII** in 47 and 15% yields, respectively¹¹.

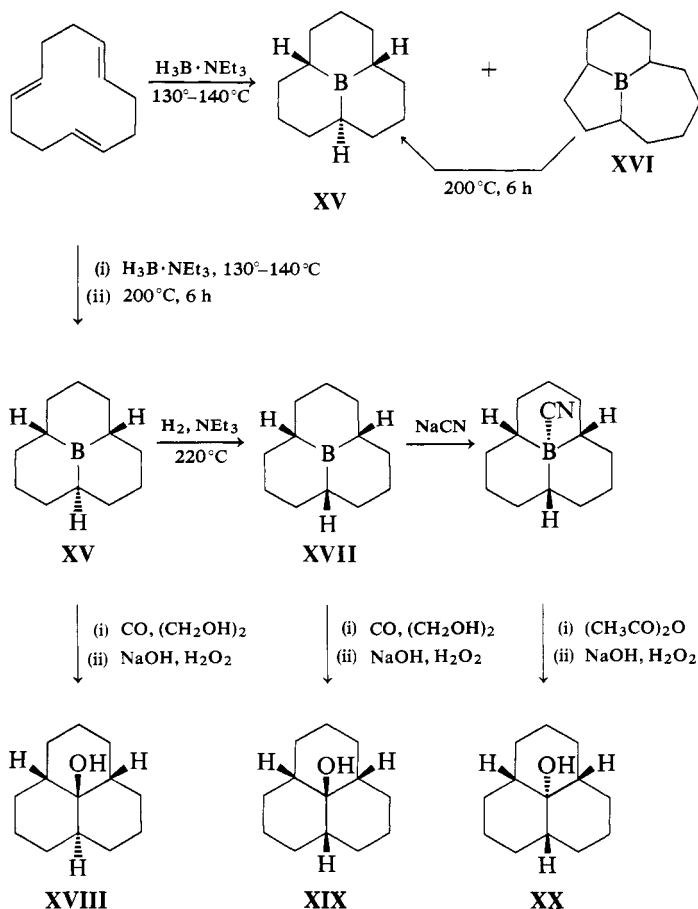
The borinane moiety is thus thermally more stable than the borepane moiety.

These results for 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene allow the courses of thermal isomerization in other cases to be predicted. Hydroboration of 1,5-cyclooctadiene yields quantitatively a 72:28 mixture of 9-borabicyclo[3.3.1]nonane (9-BBN) (**IX**) and 9-borabicyclo[4.2.1]nonane (**X**), both of which exist as dimers¹². In refluxing THF, the latter can be isomerized to 9-BBN within 1 h¹³.

Little is known about the thermal isomerization of organoboranes derived from trienes and higher polyenes. Hydroboration of 1,4,8-nonatriene and its 5-methyl derivative with $\text{H}_3\text{B}\cdot\text{THF}$ gives insoluble polymeric products. When this mixture is heated to 210–220°C, bicyclic boranes **XI** and **XIII** are formed in good yields, along with other minor bicyclic products. Carbonylation–oxidation of the bicyclic boranes provides 9-decalol (**XII**) and 10-methyl-9-decalol (**XIV**) in 73 and 46% yields, respectively, based on the initial trienes¹⁴:

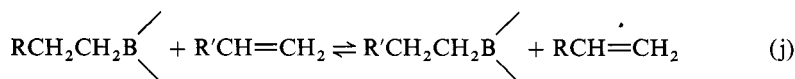


Hydroboration of 1,5,9-cyclododecatriene with $\text{H}_3\text{B}\cdot\text{THF}$ gives a polymeric product. If the hydroboration is performed at $130\text{--}140^\circ\text{C}$ using¹⁵ $\text{H}_3\text{B}\cdot\text{NEt}_3$, cis, trans-9b-boraperhydrophenalene (**XV**) and its isomers are obtained in high combined yield¹⁶. Although not fully identified, **XVI** is the major isomeric product. Heating the above mixture to 200°C for 6 h causes¹⁶ isomerization of **XVI** to **XV**. The same product can also be obtained by heating the polymer to 200°C . A much slower isomerization converting the cis, trans isomer (**XV**) into the all-cis isomer (**XVII**) may be effected¹⁵ at 200°C in the presence of H_2 and Et_3N . Triethylamine stabilizes the boron hydride intermediate. The role of H_2 is unclear. Carbonylation-oxidation of **XV**¹⁶ and **XVII**¹⁷ produces the cis, cis, trans and cis, cis, cis isomers of perhydro-9b-phenalenol, **XVIII** and **XIX**, respectively. Conversion of **XVII** into the cyanoborate anion followed by treatment with $(\text{CF}_3\text{CO})_2\text{O}$ and oxidation (Scheme 1) gives exclusively the trans, trans, trans-isomer¹⁸ **XX**.



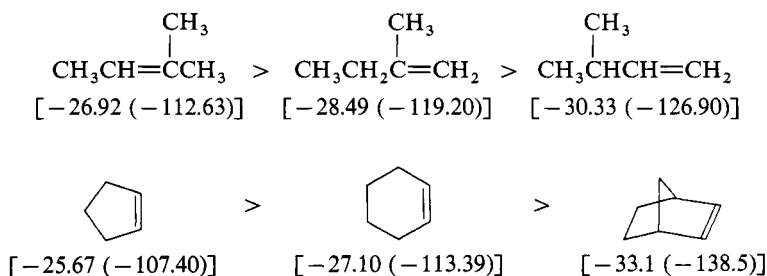
Scheme 1

If the mechanism of isomerization shown in Eq. (a) is correct, thermal treatment of an organoborane in the presence of an olefin should yield equilibrium mixtures of organoboranes, some of which are derived from the olefin added:



In this displacement an olefin replaces another olefin from an organoborane. If the olefin added is less volatile than the olefin displaced from the organoborane, the equilibrium may be shifted to produce the more volatile olefin in high yield. The rate of displacement is independent of the concentration of the displacing olefin, in agreement with the dehydroboration-rehydroboration mechanism, in which the dehydroboration is the rate-determining step¹⁹.

Some representative results of displacement of olefins from various organoboranes in refluxing diglyme using 1-decene as a displacing olefin are summarized in Table 4¹⁹. The results summarized there indicate that displacement in refluxing diglyme can proceed with little or no isomerization. The ease of displacement parallels the stability of the olefins, as measured by their heats of hydrogenation in kcal/mol (kJ/mol):



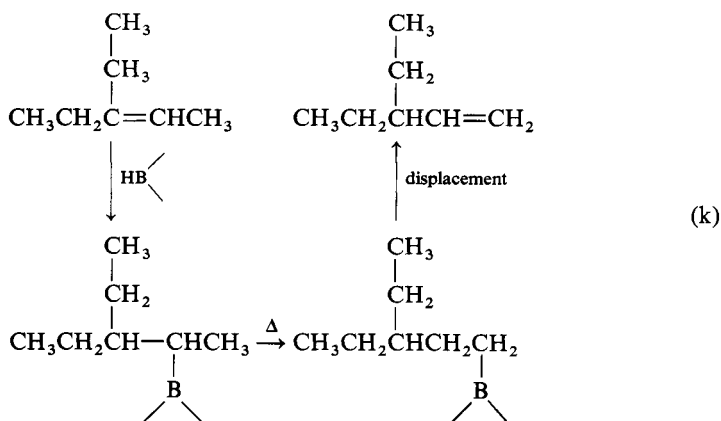
The smaller the heat of hydrogenation, the easier is the displacement reaction.

It is possible first to isomerize an organoborane and then to add an appropriate olefin to effect displacement. In this way, 2-pentene is converted in 77% yield to a 91:9

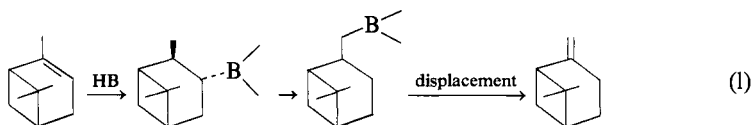
TABLE 4. DISPLACEMENT OF OLEFINS FROM ORGANOBORANES WITH 1-DECENE

Organoborane from olefin	Time (h)	Yield (%)	Olefin (%)	
			1-Olefin	2-Olefin
1-Pentene	5	76	88	12
2-Pentene	2.5	87	2	98
2,4,4-Trimethyl-1-pentene	5	89	100	0
2,4,4-Trimethyl-2-pentene	5	80		100

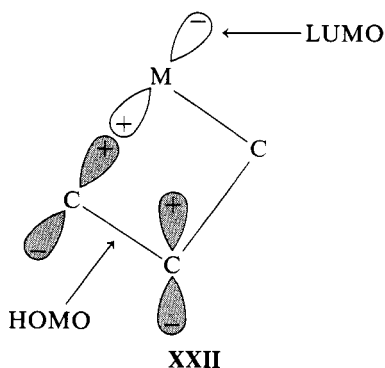
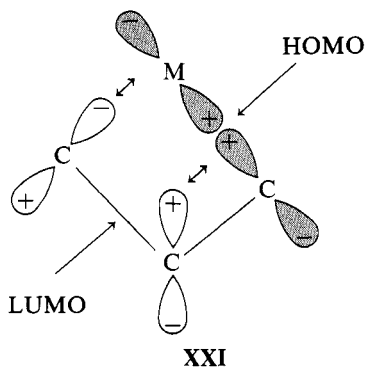
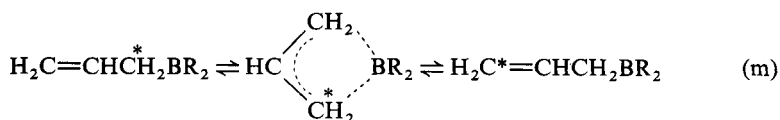
mixture of 1- and 2-pentene¹⁹. The hydroboration-isomerization-displacement sequence permits a contra-thermodynamic isomerization of olefins:



Isomerization of endocyclic olefins to exocyclic olefins is also feasible²⁰:

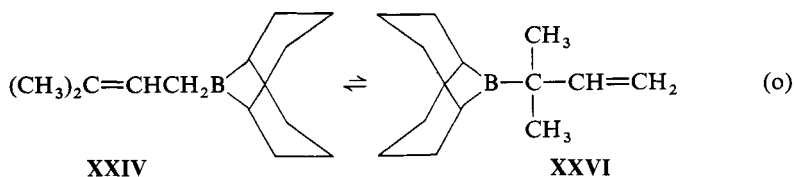
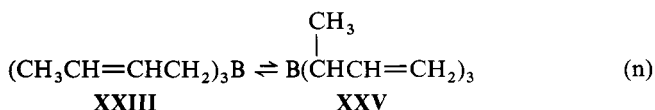


Isomerization of allylboranes proceeds not by a dehydroboration-rehydroboration mechanism that would involve the intermediacy of allenes, but by an allylic rearrangement or 1,3-metallotropy that is a symmetry-allowed concerted process. The probable HOMO-LUMO interactions suggested for the 1,3-metallotropy are shown in formulas XXI and XXII.

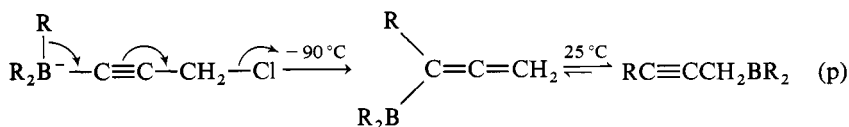


The ^1H NMR spectrum of triallylborane at or below -40°C shows a static allyl pattern, whereas that taken at 135°C shows an AX_4 pattern^{21–23}. The latter indicates that the four α - and γ -H atoms are equivalent by virtue of rapid allylic rearrangement accompanied by rapid rotation about the C—C single bonds. The activation energy for the allylic rearrangement is estimated to be 10 ± 1 kcal/mol (42 ± 4 kJ/mol). Because the rate of exchange is independent of concentration, the allylic rearrangement is an intramolecular process Eq. (m). Donor solvents, e.g., THF and pyridine (py), retard the allylic rearrangement. According to ^1H NMR study of triallylborane·py, the allylic rearrangement occurs via dissociation of the complex into free triallylborane; this supports the interpretation that the facile allylic rearrangement arises from the availability of the empty p orbital of boron, which makes the otherwise symmetry-forbidden, concerted process favorable.

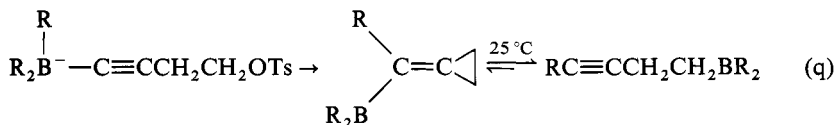
The equilibrium position of the allylic rearrangement depends on the steric requirements of the α - and γ -carbons. Thus, e.g., the ^1H -NMR spectra of tricrotylborane^{21–23} (XXIII) and B-isoprenyl-9-BBN²⁴ (XXIV) do not reveal the presence of their regioisomers XXV and XXVI. These observations, however, do not preclude allylic rearrangement of XXIII and XXIV. Variable-T NMR examination of B-crotyl-9-BBN and XXIV indicates that the cis-trans isomerization arising via allylic rearrangement is rapid on that time scale at 40 and 140°C , respectively²⁴:



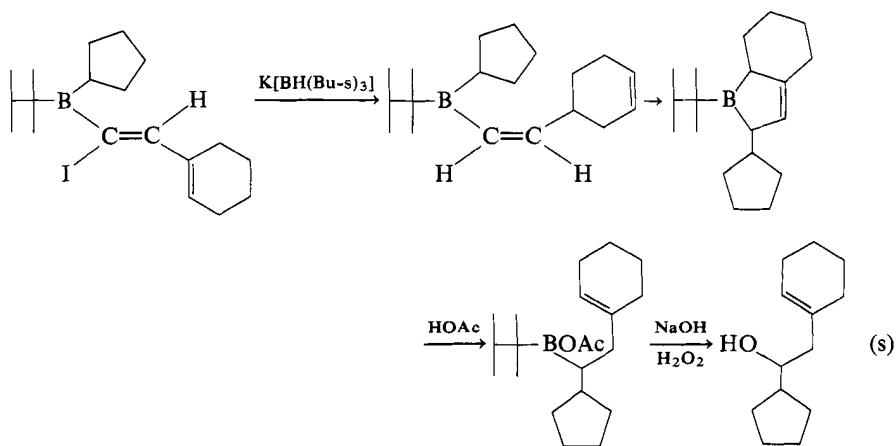
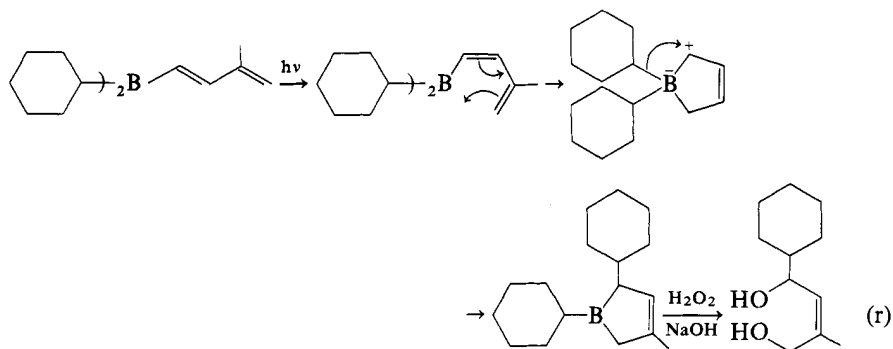
Allylic rearrangement also provides a means of interconverting propargylic and allenic boranes²⁵.



A homologous version of Eq. (k) is also known²⁶:



Other isomerizations of organoboranes are conceivable; e.g., the following isomerization of dienyloboranes involves the 1,2-migration of zwitterionic species^{27,28}:



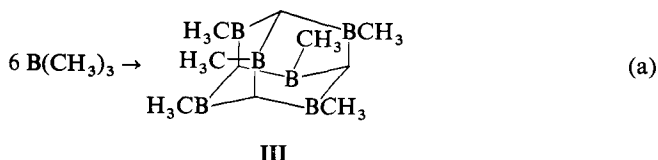
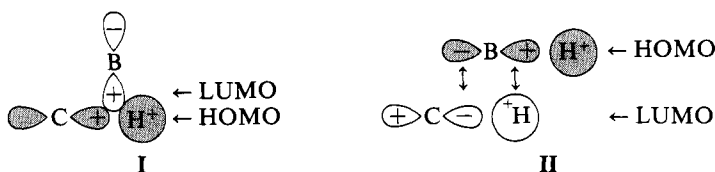
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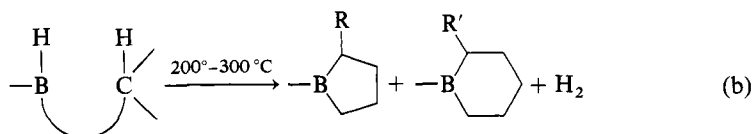
5.3.2.6.3. by Pyrolytic Elimination of H₂.

Pyrolysis of organoboranes at $\geq 200^\circ\text{C}$ can lead to substitution of hydrogen with boron accompanied by evolution of H₂ [see Eq. (e), §5.3.2.6]^{1,2}. Little is known about the mechanism, but it does not involve radicals. A single-bonded version of hydroboration may be taking place on the C—H bond, in which the HOMO—LUMO interactions shown in **I** and **II** are important.



Pyrolysis of trimethylborane gives **III**. Triethylborane yields ethylene and methylethylboranes, and triisobutylborane gives isobutylene and methylpropylboranes^{3,4}. Cleavage of C—C bonds occurs here, either intra- or intermolecularly.

Alkylboranes containing a four-carbon chain or longer can undergo intramolecular substitution that is more facile than the reactions of smaller alkylboranes mentioned above. At $200\text{--}300^\circ\text{C}$ boracyclanes containing five- and six-membered rings may be obtained in high yields:



The reaction requires the generation of boron hydrides as reactive species.

5.3. Formation of Bonds

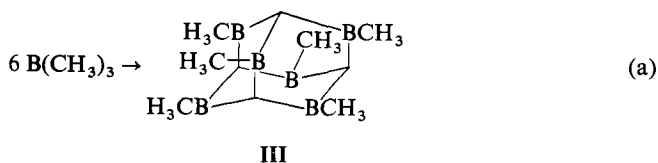
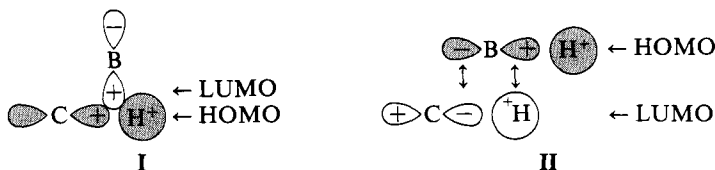
5.3.2. Formation of Carbon—Boron Bonds

5.3.2.6. from Organoboranes

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18. A. Pelter, P. J. Maddocks, K. Smith, *J. Chem. Soc., Chem. Commun.*, 805 (1978).
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20. H. C. Brown, M. V. Bhatt, T. Munekata, G. Zweifel, *J. Am. Chem. Soc.*, **89**, 567 (1967).
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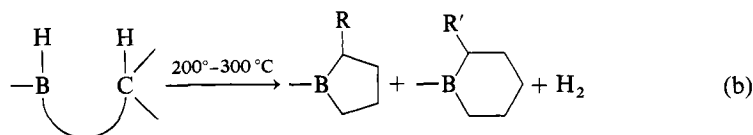
5.3.2.6.3. by Pyrolytic Elimination of H_2 .

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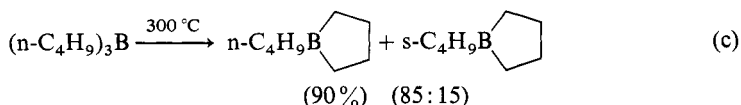
Pyrolysis of trimethylborane gives III. Triethylborane yields ethylene and methylethylboranes, and triisobutylborane gives isobutylene and methylpropylboranes^{3,4}. Cleavage of C—C bonds occurs here, either intra- or intermolecularly.

Alkylboranes containing a four-carbon chain or longer can undergo intramolecular substitution that is more facile than the reactions of smaller alkylboranes mentioned above. At 200–300°C boracyclanes containing five- and six-membered rings may be obtained in high yields:



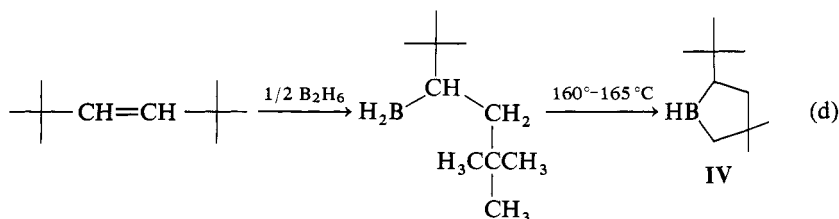
The reaction requires the generation of boron hydrides as reactive species.

Tri-n-butylborane gives an 85:15 mixture of B-(n-butyl)borolane and B-(s-butyl)-borolane in 90% yield along with butenes and H₂:

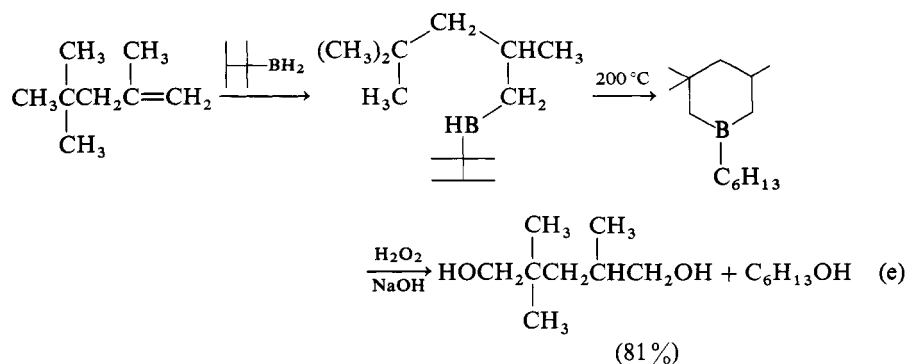


Tri-n-hexylborane reacts at ca. 200°C with 2 equiv H₃B·NEt₃ to give mixed B-hexylboracyclanes. Their oxidation with alkaline H₂O₂ produces 1,4- and 1,5-hexanediols and 1-hexanol as the major products. Small amounts of 1,6-hexanediol and 2-hexanol are also obtained^{5,6}.

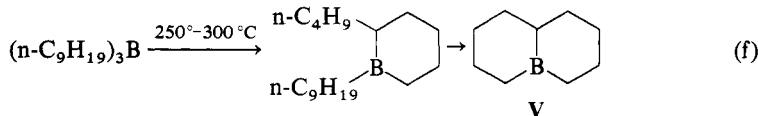
The use of preformed boron hydrides is advantageous. Thus, treatment of 1,2-di-butylethylene with 0.5 equiv. B₂H₆ followed by heating the mixture for 20 h at 160–165°C gives⁷ IV:



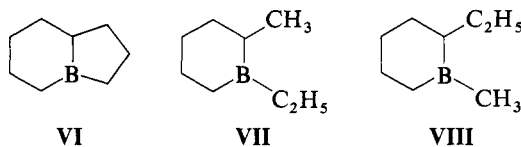
Similarly, the hydroboration of 2,4,4-trimethyl-pentene with 1 equiv 2,3-dimethyl-2-butyl (thexyl) borane followed by heating the mixture at 200°C gives, after oxidation, 2,4,4-trimethyl-1,5-pentanediol in 81% yield⁸:



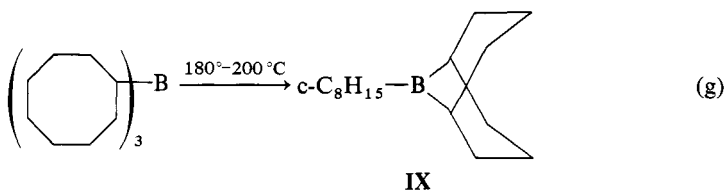
Alkylboranes containing chains of ≤ 8 carbons can be converted to bicyclic boracyclanes. Thus, pyrolysis of tri-n-nonylborane at 250–300°C produces 9-boradecalin (V) in 80% yields⁹.



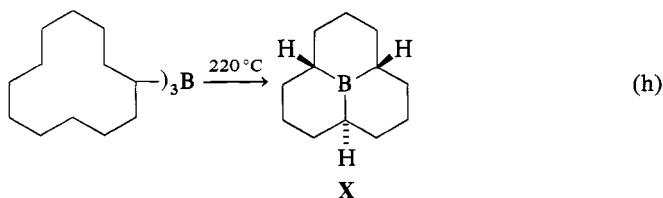
Tri-*n*-octylborane can also be converted to 8-borahydrindane (VI), albeit in low yield⁵. This reaction is accompanied by C—C bond cleavage producing VII and VIII.



Cycloalkylboranes containing rings of ≥ 8 carbons can produce bicyclic or polycyclic boracyclanes. At 180°–200°C tricyclooctylborane produces B-cyclooctyl-9-BBN (IX)¹⁰.

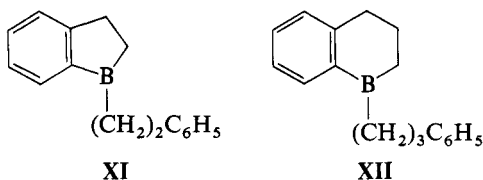


where 9-BBN is 9-borabicyclo[3.3.1]nonane. When heated to 220°C, tricyclodocylborane yields *cis*,*trans*-perhydro-9B-boraphenalene (X) as the major product¹⁰. The original stereochemical assignment is erroneous and must be reversed^{11,12}:

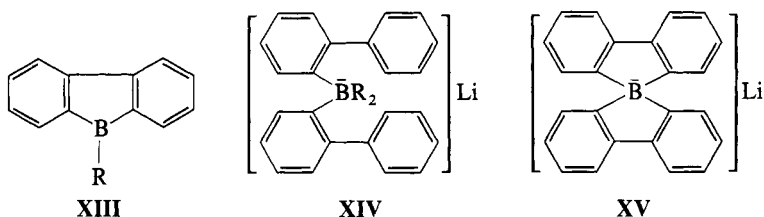


Cycloalkylboranes containing cycloalkane rings smaller than cyclooctane do not give bicyclic boracyclanes. The courses of such reactions are unclear, but they are more complex than the examples shown above.

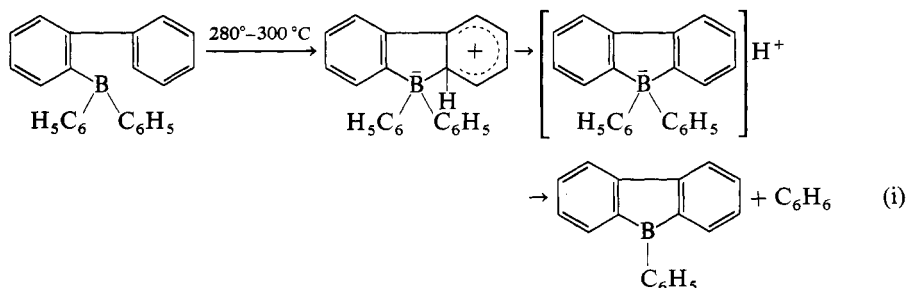
Pyrolysis of aralkylboranes producing 1-boraindanes and 1-boratetralins proceeds more readily than the corresponding cyclization reactions of alkylboranes. Tri-2-phenethylborane and tris-3-phenylpropylborane at 180–230°C give XI and XII, respectively, in > 90% yields^{7,13}.



On heating 2-biphenyldialkylboranes or 2-biphenyldiarylboranes, 9-borafluorene derivatives (XIII) can be obtained in good yields¹⁴.



The pyrolysis of the dialkyl-substituted derivatives proceeds at 180°C, whereas that of the aryl analogues occurs only at 280–300°C, indicating that the two cases likely involve different mechanisms. The latter reaction may involve electrophilic aromatic substitution-protonolysis:



Even 2-biphenylborates (XIV) may be converted¹⁵ to XV.

Certain carborane-forming reactions may involve related pyrolytic processes¹⁶ (see §5.3.2.7).

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5.3.2.6.4. by Addition of Olefinic and Acetylenic Linkages (Carbaboration).

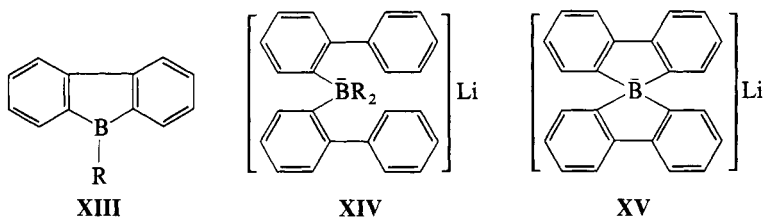
In contrast to the facile hydroboration, the corresponding carbaboration involving four-electron processes does not occur readily. The short B—C bond, relative to those metal—carbon bonds that are known to participate in the four-electron carbometallation, may impose steric hindrance to carbaboration. The presence of an empty p orbital,

5.3. Formation of Bonds

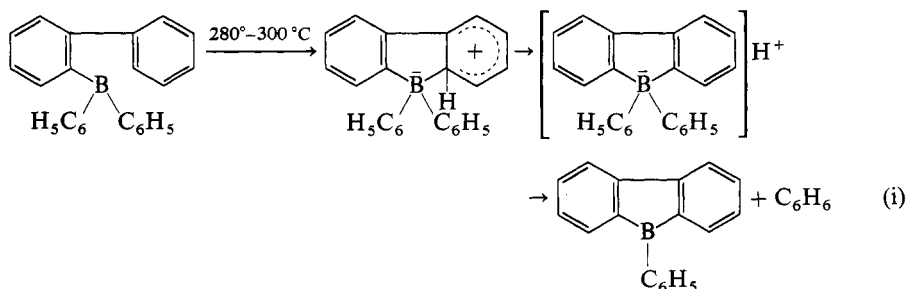
5.3.2. Formation of Carbon—Boron Bonds

5.3.2.6. from Organoboranes

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The pyrolysis of the dialkyl-substituted derivatives proceeds at 180°C, whereas that of the aryl analogues occurs only at 280–300°C, indicating that the two cases likely involve different mechanisms. The latter reaction may involve electrophilic aromatic substitution-protonolysis:



Even 2-biphenylborates (XIV) may be converted¹⁵ to XV.

Certain carborane-forming reactions may involve related pyrolytic processes¹⁶ (see §5.3.2.7).

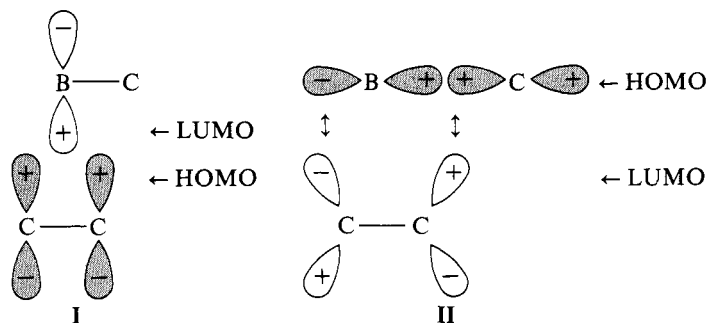
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1. R. Köster, *Adv. Organomet. Chem.*, **2**, 257 (1964).
2. R. Köster, *Prog. Boron Chem.*, **1**, 289 (1964).
3. M. P. Brown, A. K. Holliday, G. M. Way, *J. Chem. Soc., Dalton Trans.*, 148 (1975); see also, J. Goubeau, R. Epple, *Chem. Ber.*, **90**, 171 (1957).
4. R. Köster, W. Larbig, *Angew. Chem.*, **73**, 620 (1961).
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9. R. Köster, G. Rotermund, *Angew. Chem.*, **72**, 563 (1960).
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16. For a review see R. N. Grimes, *Carboranes*, Academic Press, New York, 1970.

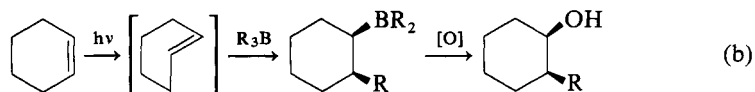
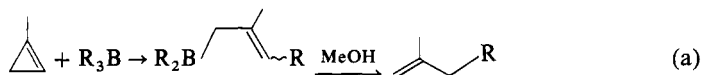
5.3.2.6.4. by Addition of Olefinic and Acetylenic Linkages (Carboboration).

In contrast to the facile hydroboration, the corresponding carboboration involving four-electron processes does not occur readily. The short B—C bond, relative to those metal—carbon bonds that are known to participate in the four-electron carbometallation, may impose steric hindrance to carboboration. The presence of an empty p orbital,

however, makes the four-electron carboboration a symmetry-allowed process, in which the HOMO-LUMO interactions shown in **I** and **II** are important:

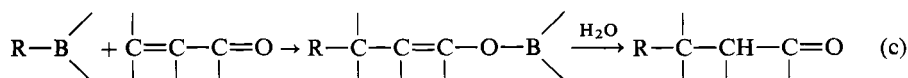


Examples of carboborations involving highly strained olefins are known^{1,2}:

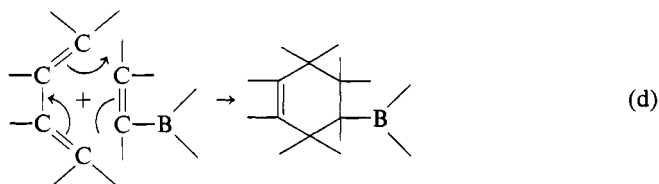


Although not discussed here, reactions of alkynes with organoboranes leading to the formation of carboranes are also known³ (see §5.3.2.7).

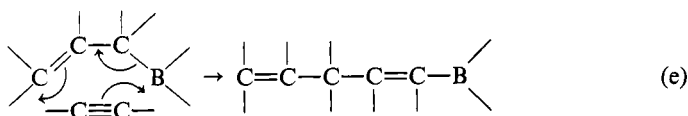
Unlike the four-electron carboboration, some reactions of organoboranes proceed via concerted six-electron processes. Such reactions include (1) conjugate addition of organoboranes:



(2) Addition of alkenyl- and alkynylboranes:

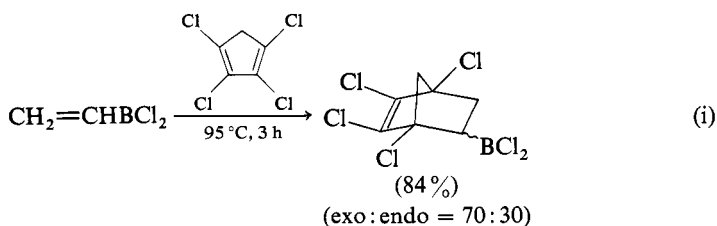
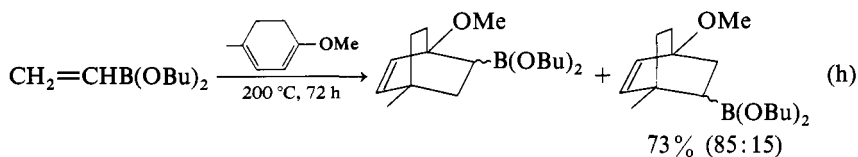
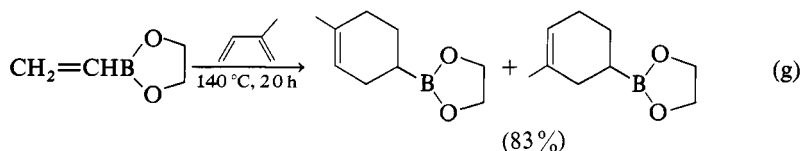
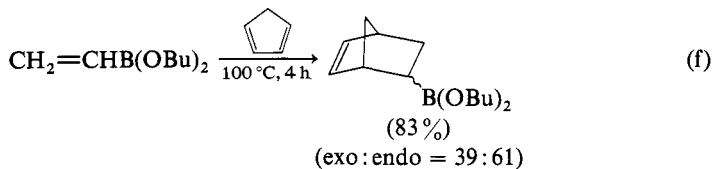


and (3) carboboration of allylic and propargylic boranes:

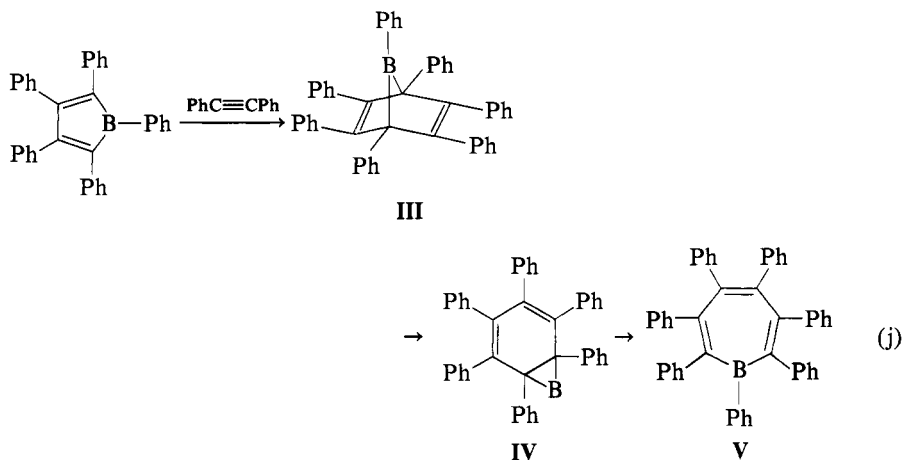


In the first two of these three reactions, organoboranes act as two-electron reactants, whereas they serve as four-electron reactants in the allylic and propargylic carboboration.

Because conjugate addition^{3,5} does not generate new B—C bonds, it is not discussed here. Addition of alkenyl- and alkynylboranes does not involve the reaction of the B—C bond. It does, however, modify the nature of the B—C bond. Various dialkoxy-⁶⁻⁹ and dihaloalkenylboranes⁹ react with dienes to form the addition adducts:

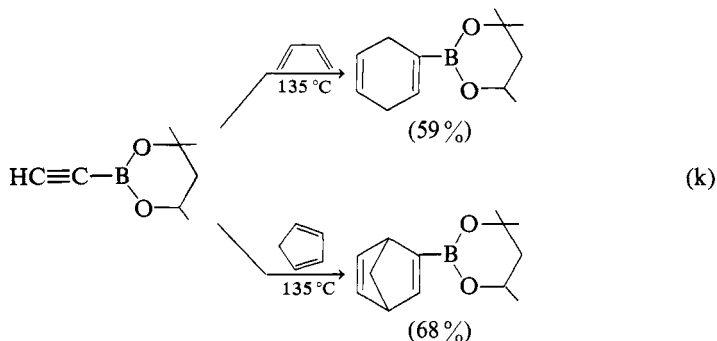


Pentaphenylborole can participate as a diene in addition with diphenyl acetylene^{11,12}:

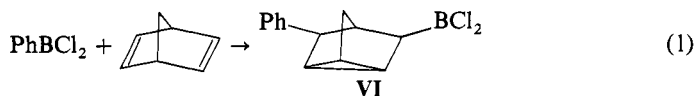


The bridged bicyclic adduct **III** can undergo an allylic rearrangement to form **IV**, which in turn undergoes a rearrangement to produce **V**.

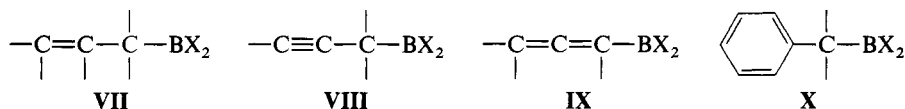
Addition of alkynylboranes provides a route to functionalized 1,4-cyclohexadienes^{9,13}:



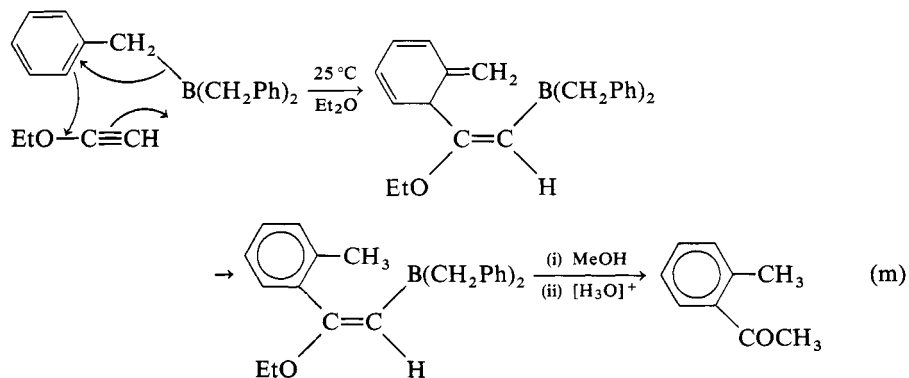
Phenyldichloroborane reacts with norbornadiene to form **VI** by an unknown mechanism¹⁴:



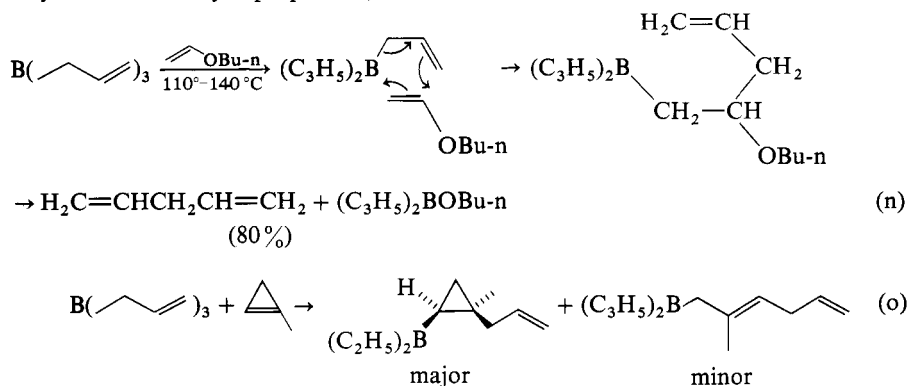
β,γ -Unsaturated organoboranes, e.g., **VII-X**, in principle can participate in carboboration with acetylenes and olefins; it proceeds via symmetry-allowed six-electron processes, although there is no well-documented example of the carboboration of **VIII** or **IX**.



The scope of the carboboration of benzylboranes (**X**) is also limited; however, the following example¹⁵ suggests that it may be a useful synthesis:



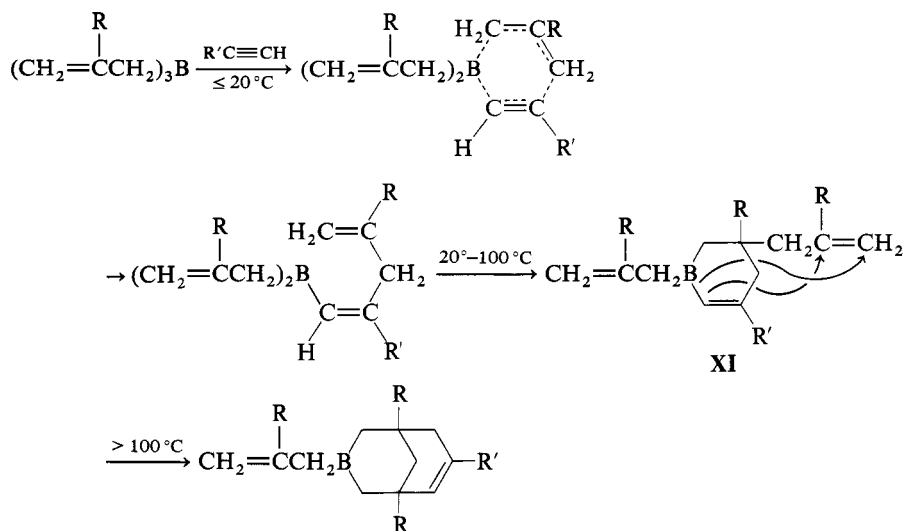
The carbometallation of allylboranes is known^{16–18}. Alkenes are less reactive than alkynes or allenes in reaction with allylboranes. Only highly reactive alkenes, such as vinyl ethers¹⁸ and cyclopropenes²⁰, are used.



The reactions of allylboranes with alkynes can proceed in three discrete steps. The first involves the addition of the allyl-boron bond to $\text{C}\equiv\text{C}$ which takes place at or below RT. The second allyl-boron bond can then add intramolecularly to $\text{C}=\text{C}$ in the δ,ϵ -position at $20^\circ-100^\circ\text{C}$ to form boracyclohexene derivatives (XI). Finally, at $\geq 100^\circ\text{C}$, the alkenyl-boron bond adds across $\text{C}=\text{C}$ in the δ,ϵ -position to form bicyclic boracyclanes (XII) as in Scheme 1.

The structures of XI and XII are established, in part, through further transformations, such as those shown in Schemes 2 and 3.

The reaction of allylboranes with allenes²¹ proceeds analogously to that with alkynes, although this reaction requires higher T ($> 150^\circ\text{C}$). The borons may be placed at



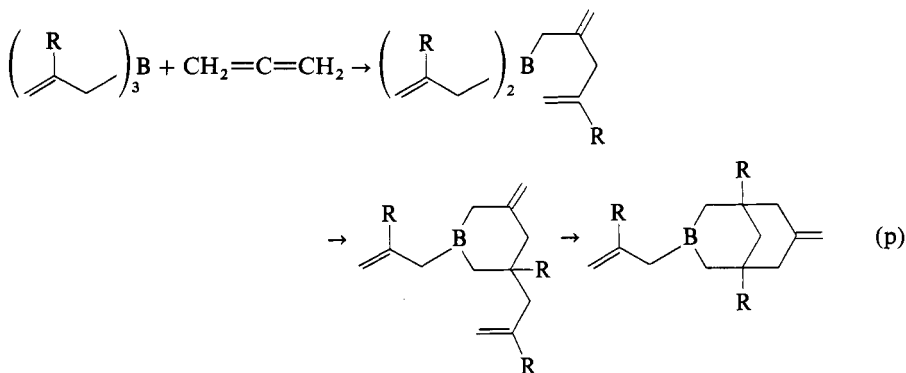
where R,R' = H, alkyl, aryl.

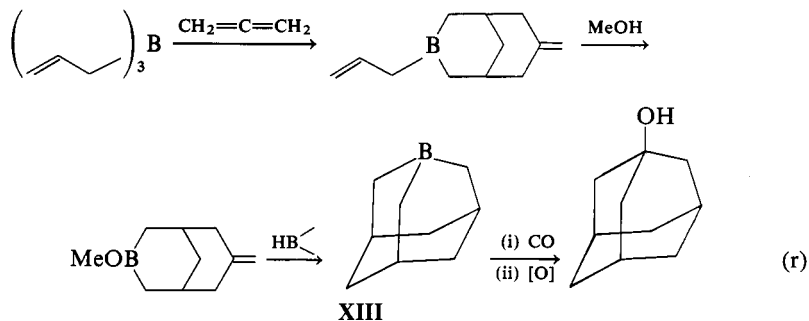
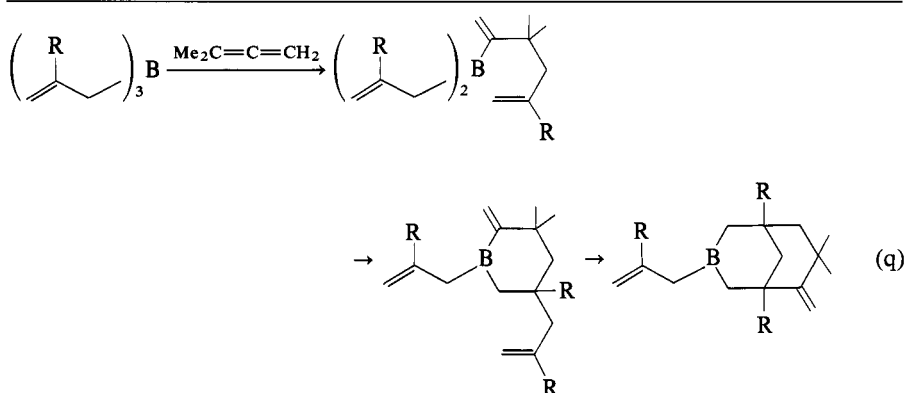
XII

Scheme 1

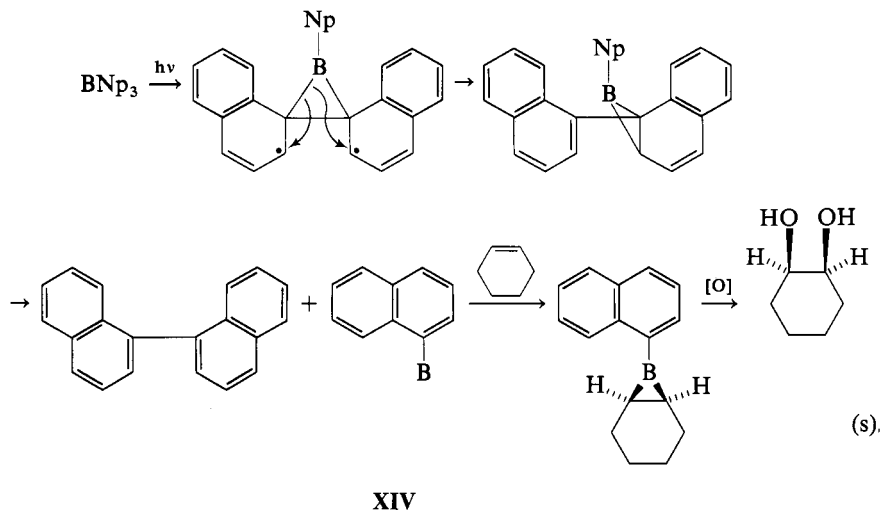
Scheme 2

Scheme 3





The reaction of tri-1-naphthylborane with cyclohexene under photolytic conditions²² does not fall into any of the types discussed above. The reaction involves the boron version of the di- π -methane rearrangement followed by extrusion of 1-naphthylboryne (XIV) and its addition to cyclohexene:



where Np is naphthyl. Its novel features include the generation and the addition reaction of organoboryne species.

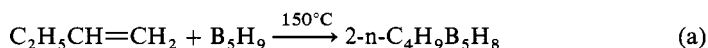
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6. D. S. Matteson, J. O. Waldbillig, *J. Org. Chem.*, 28, 366 (1963).
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16. B. M. Mikhailov, *Organomet. Chem. Rev.*, A, 8, 1 (1972).
17. B. M. Mikhailov, *Intrasci. Chem. Rep.*, 7, 191 (1973).
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20. Yu. N. Bubnov, O. A. Nesmeyanova, T. Yu. Rudashevskaya, B. M. Mikhailov, B. A. Kazansky, *Tetrahedron Lett.*, 2153 (1971).
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5.3.2.7. from Larger Boranes and Carboranes

5.3.2.7.1. by Hydroboration of a Polyborane.

Reaction of B_5H_9 with olefins at elevated T gives good conversions but poor yields of 2-alkylpentaboranes, the result of a simple hydroboration:



Ethylene and B_5H_{11} similarly form¹ both $C_2H_5B_5H_{10}$ and $(C_2H_5)_2B_5H_9$. Hydroboration of cyclohexene with $B_{10}H_{12}[S(CH_3)_2]_2$ produces² 9-cyclohexyl-5(7)-dimethylsulfide-nido-decaborane(11), $B_{10}H_{11}(C_6H_{11})[S(CH_3)_2]$. Also, propylene reacts³ with $(H_3O)_2B_{12}H_{12} \cdot 5 H_2O$ to afford³ $[C_3H_7-B_{12}H_{11}]^{2-}$.

A B-1-propenyl derivative of 1,5- $C_2B_3H_5$ is the product from propyne and the parent, trigonal-bipyramidal, closo-carborane:⁴



The reaction of pentaborane (9) under mild conditions with $RC \equiv CR$ ($R = H, CH_3$) in the presence of catalytic amounts of $Ir(CO)Cl[P(C_6H_5)_3]_2$ results in the respective alkenylpentaboranes, 2- $CHR=CR'B_5H_8$. The B—H adds to the alkyne in cis fashion, and propyne adds hydrogen to the carbon atom bearing the least hydrogen. Similarly, $(RC_2R')Co_2(CO)_6$ ($R, R' = H$ or CH_3) complexes also activate acetylenes for B—H additions with B_5H_9 ⁵, as well as with the small carboranes⁶ 1,5- $C_2B_3H_5$, 1,6- $C_2B_4H_6$,

5.3. Formation of Bonds

5.3.2. Formation of Carbon—Boron Bonds

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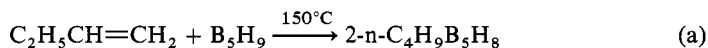
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2,4- $C_2B_5H_7$ and 2,3- $C_2B_4H_8$; however, in contrast to the results with $Ir(CO)Cl[P(C_6H_5)_3]_2$, terminal alkynes add hydrogen to the carbon with the most hydrogen.⁵

Alkyl derivatives of the nido-carborane, 2- CB_5H_9 , are found as side products from the thermal (200°C) reaction between pentaborane (9) and acetylenes (see §5.3.2.7.3).⁷ These alkyl derivatives of 2- CB_5H_9 are formed from the internal 1,1 addition of two B—H bonds of the polyborane to the acetylene.

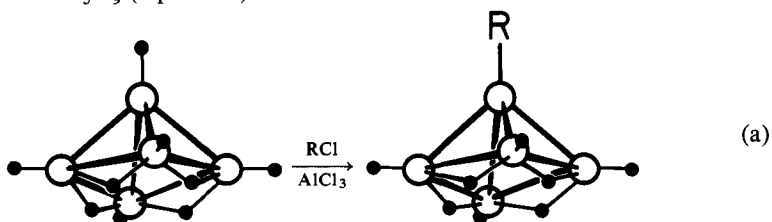
The gas-phase photolysis of hexafluoroacetone and a polyborane (B_5H_9 or 2,4- $C_2B_5H_7$) produces cage, boron-bonded $-C(CF_3)_2OH$ derivatives of these polyboranes⁸.

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1. T. Onak, *Organoborane Chemistry*, Academic Press, New York, 1975.
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5.3.2.7.2. by Modified Metal Halide-Catalyzed Alkylations with Organic Halides at a Boron Site.

Alkylation of B_5H_9 (1 position):



and of $B_{10}H_{14}$ (2,4 and 1,3 positions), is effected using organic halides and metal halide catalysts. Although alkyl halides or olefins are normally the organic reactant, $(RO)_3B$, alkyl ethers and alkylsilicates are also utilized¹.

Reaction of B_5H_9 with $(CH_3)_3SiCH_2Cl$ in the presence of $AlCl_3$ gives 1- $CH_3B_5H_8$ and $(CH_3)_3SiCl$ quantitatively, whereas use of Cl_3SiCH_2Cl as the alkylating agent affords² primarily 1- $Cl_3SiCH_2B_5H_8$.

B-Mono- and polymethylation of pentagonal-bipyramidal, closo-2,4- $C_2B_5H_7$ with CH_3Cl in the presence of $AlCl_3$ follow a positional preference 5,6 > 1,7 > 3, in agreement with an electrophilic substitution mechanism³. B-alkylation of closo-1,2- and 1,7- $C_2B_{10}H_{12}$ under similar conditions also occurs⁴⁻⁸.

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1. T. Onak, *Organoborane Chemistry*, Academic Press, New York, NY, 1975.
2. J. B. Leach, G. Oates, J. B. Handley, A. P. Fung, T. Onak, *J. Chem. Soc., Dalton Trans.*, 819 (1977).
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4. L. I. Zakharkin, I. V. Pisareva, R. Kh. Bikkineev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 641 (1977).
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5.3. Formation of Bonds

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5.3.2. Formation of Carbon—Boron Bonds

5.3.2.7. from Larger Boranes and Carboranes

2,4- $C_2B_5H_7$ and 2,3- $C_2B_4H_8$; however, in contrast to the results with $Ir(CO)Cl[P(C_6H_5)_3]_2$, terminal alkynes add hydrogen to the carbon with the most hydrogen.⁵

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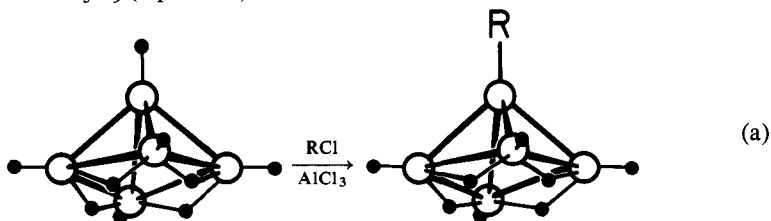
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2. E. I. Tolpin, E. Mizusawa, D. S. Becker, V. Venzel, *Inorg. Chem.*, **19**, 1182 (1980).
3. E. L. Muetterties, W. H. Knoth, *Polyhedral Boranes*, Marcel Dekker, New York, 1968.
4. A. B. Burg, T. J. Reilly, *Inorg. Chem.*, **11**, 1962 (1972).
5. R. Wilczynski, L. G. Sneddon, *Inorg. Chem.*, **20**, 3955 (1981).
6. R. Wilczynski, L. G. Sneddon, *Inorg. Chem.*, **21**, 506 (1982).
7. T. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966).
8. R. J. Astheimes, L. G. Sneddon, *Inorg. Chem.*, **23**, 3207 (1984).

5.3.2.7.2. by Modified Metal Halide-Catalyzed Alkylations with Organic Halides at a Boron Site.

Alkylation of B_5H_9 (1 position):



and of $B_{10}H_{14}$ (2,4 and 1,3 positions), is effected using organic halides and metal halide catalysts. Although alkyl halides or olefins are normally the organic reactant, $(RO)_3B$, alkyl ethers and alkylsilicates are also utilized¹.

Reaction of B_5H_9 with $(CH_3)_3SiCH_2Cl$ in the presence of $AlCl_3$ gives 1- $CH_3B_5H_8$ and $(CH_3)_3SiCl$ quantitatively, whereas use of Cl_3SiCH_2Cl as the alkylating agent affords² primarily 1- $Cl_3SiCH_2B_5H_8$.

B-Mono- and polymethylation of pentagonal-bipyramidal, closo-2,4- $C_2B_5H_7$ with CH_3Cl in the presence of $AlCl_3$ follow a positional preference 5,6 > 1,7 > 3, in agreement with an electrophilic substitution mechanism³. B-alkylation of closo-1,2- and 1,7- $C_2B_{10}H_{12}$ under similar conditions also occurs⁴⁻⁸.

(T. ONAK)

1. T. Onak, *Organoborane Chemistry*, Academic Press, New York, NY, 1975.
2. J. B. Leach, G. Oates, J. B. Handley, A. P. Fung, T. Onak, *J. Chem. Soc., Dalton Trans.*, 819 (1977).
3. J. F. Ditter, E. B. Klusmann, R. E. Williams, T. Onak, *Inorg. Chem.*, **15**, 1063 (1976).
4. L. I. Zakharkin, I. V. Pisareva, R. Kh. Bikkineev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 641 (1977).
5. L. I. Zakharkin, A. I. Kovredov, V. A. Ol'shevskaya, S. V. Vitt, *J. Gen. Chem. USSR (Engl. Transl.)*, **55**, 1019 (1985).

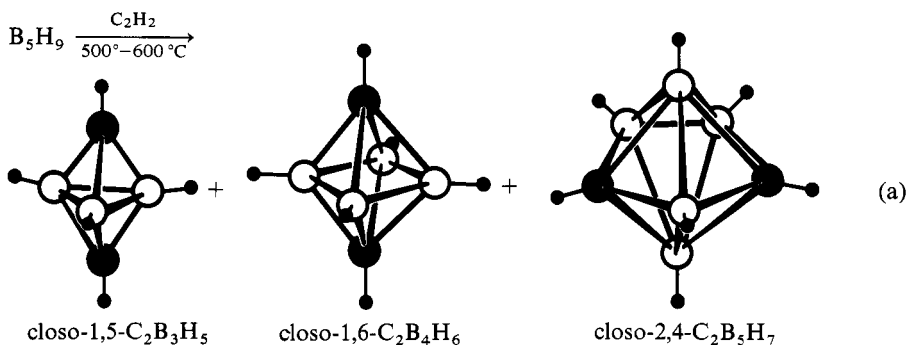
6. D. Albagli, G. X. Zheng, M. Jones, *Inorg. Chem.*, 25, 129 (1986).

7. L. I. Zakharkin, A. I. Kovredov, V. A. Ol'shevskaya, S. V. Vitt, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1528 (1983).

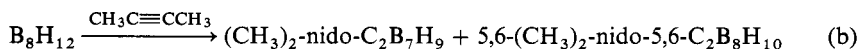
8. J. Plešek, Z. Plzak, J. Struchlik, S. Hermanek, *Coll. Czech. Chem. Commun.*, 46, 1748 (1981).

5.3.2.7.3. by B,B Addition of Polyboranes to Alkynes.

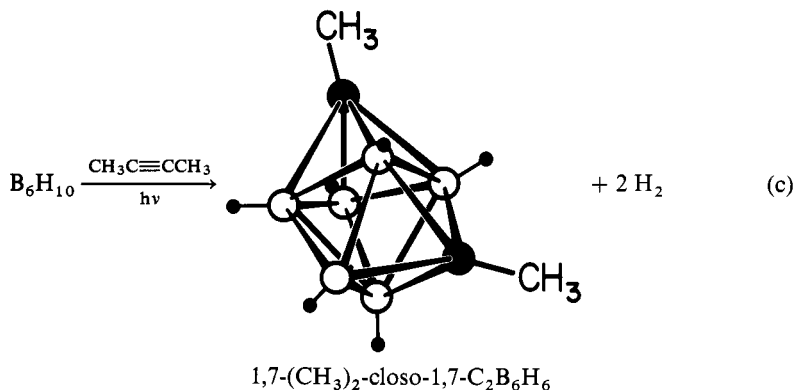
The construction of C—B bonds in carboranes is effected by reaction of alkynes with polyboron hydrides. High-T and electric discharge-induced reactions between these reagents yield closo cage systems, whereas milder conditions can lead to nido-carboranes.¹ The preferred route to the parent closo-1,6- $C_2B_4H_6$ and -2,4- $C_2B_5H_7$ compounds involves the direct thermal reaction (500–600°C) of pentaborane(9) and acetylene in a continuous-flow system. Also formed² is the smallest known closo-carborane, 1,5- $C_2B_3H_5$, in which the combined yields of products approach 70% and the product distribution of $C_2B_3H_7:C_2B_4H_6:C_2B_3H_5$ is ca. 5:5:1:



The only preparation^{3,4} of the 2,3 isomer of closo- $C_2B_5H_7$ employs octaborane(12) with alkynes³, which is accompanied by the production of the C,C'-dimethyl derivatives of both $C_2B_7H_{11}$ and 5,6- $C_2B_8H_{12}$:



A 1,7-dimethyl derivative of closo-1,7- $C_2B_6H_8$ is formed in low yield from B_6H_{10} and dimethylacetylene at ca. 200°C; with irradiation, the yield is improved⁵:



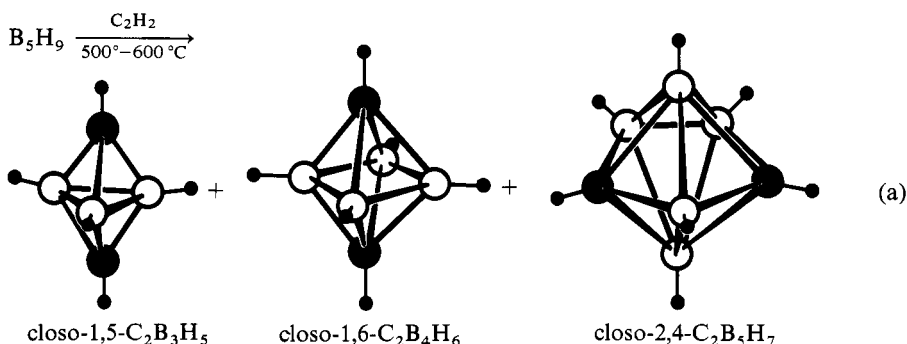
6. D. Albagli, G. X. Zheng, M. Jones, *Inorg. Chem.*, 25, 129 (1986).

7. L. I. Zakharkin, A. I. Kovredov, V. A. Ol'shevskaya, S. V. Vitt, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1528 (1983).

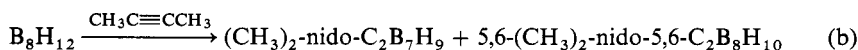
8. J. Plešek, Z. Plzak, J. Struchlik, S. Hermanek, *Coll. Czech. Chem. Commun.*, 46, 1748 (1981).

5.3.2.7.3. by B,B Addition of Polyboranes to Alkynes.

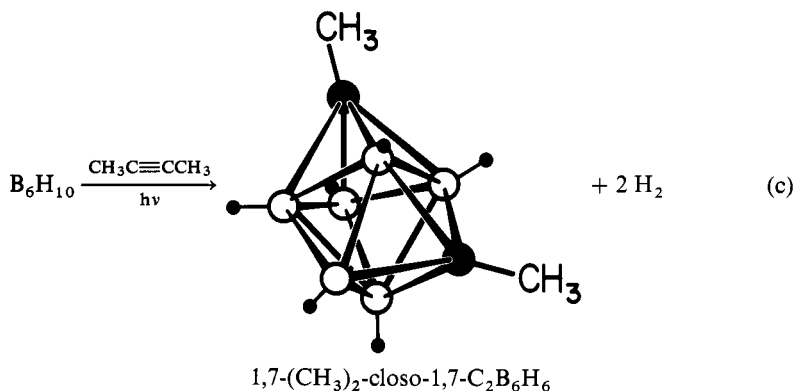
The construction of C—B bonds in carboranes is effected by reaction of alkynes with polyboron hydrides. High-T and electric discharge-induced reactions between these reagents yield closo cage systems, whereas milder conditions can lead to nido-carboranes.¹ The preferred route to the parent closo-1,6-C₂B₄H₆ and -2,4-C₂B₅H₇ compounds involves the direct thermal reaction (500–600°C) of pentaborane(9) and acetylene in a continuous-flow system. Also formed² is the smallest known closo-carborane, 1,5-C₂B₃H₅, in which the combined yields of products approach 70% and the product distribution of C₂B₃H₇:C₂B₄H₆:C₂B₅H₅ is ca. 5:5:1:



The only preparation^{3,4} of the 2,3 isomer of closo-C₂B₅H₇, employs octaborane(12) with alkynes³, which is accompanied by the production of the C,C'-dimethyl derivatives of both C₂B₇H₁₁ and 5,6-C₂B₈H₁₂:



A 1,7-dimethyl derivative of closo-1,7-C₂B₆H₈ is formed in low yield from B₆H₁₀ and dimethylacetylene at ca. 200°C; with irradiation, the yield is improved⁵:



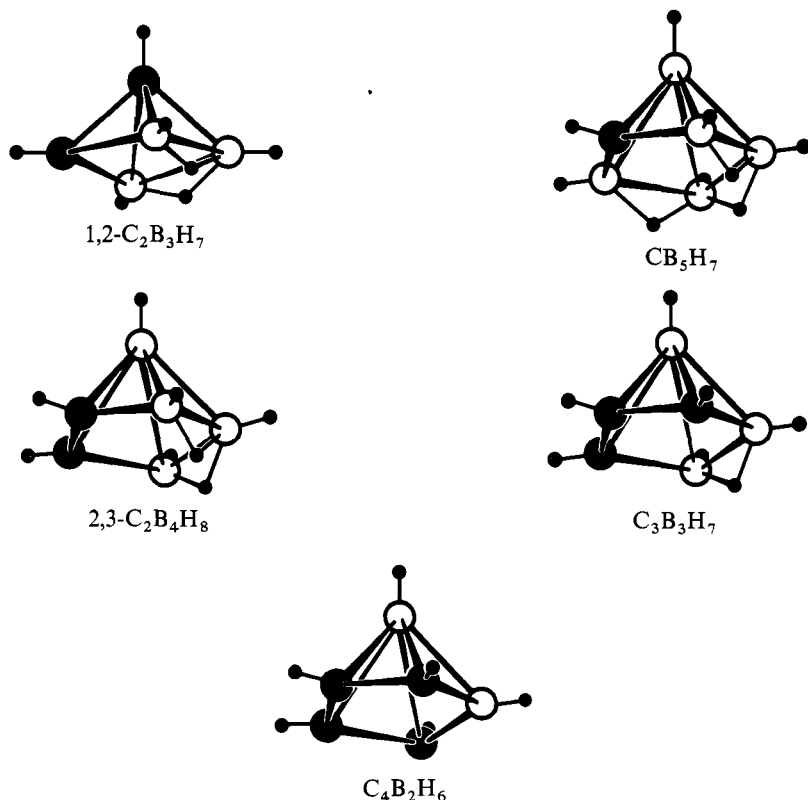
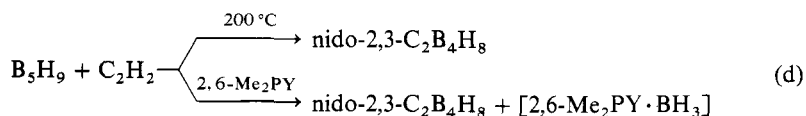


Figure 1. The Nido-compounds. ●, carbon; ○, boron; •, hydrogen.

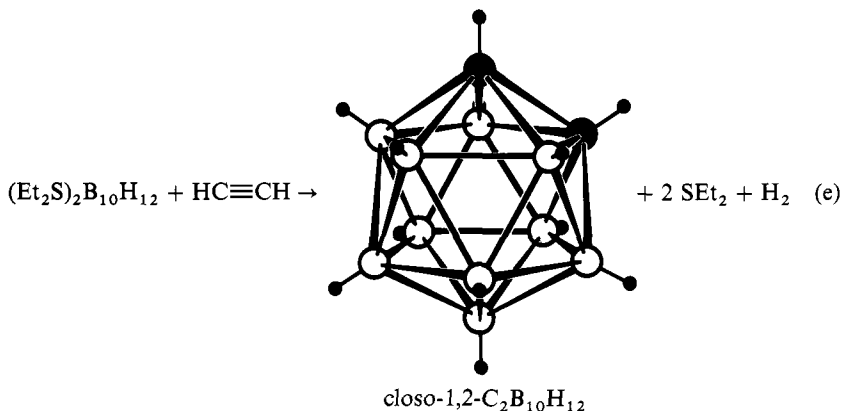
A nido-carborane mixture, formed from B_4H_{10} with acetylenes under mild conditions, includes alkyl derivatives of nido- CB_5H_9 , nido- $\text{C}_2\text{B}_4\text{H}_8$, nido-2,3,4- $\text{C}_3\text{B}_3\text{H}_7$, nido- $\text{C}_4\text{B}_2\text{H}_6$ as well as nido-1,2- $\text{C}_2\text{B}_3\text{H}_7$ (Fig. 1)⁶⁻⁸. The reaction of the square-pyramidal nido-1,2- $\text{C}_2\text{B}_3\text{H}_7$ with $\text{HC}\equiv\text{CH}$ produces pentagonal-pyramidal 2,3,4,5- $\text{C}_4\text{B}_2\text{H}_6$ (Fig. 1). Using $\text{CH}_3\text{C}\equiv\text{CH}$ in place of $\text{HC}\equiv\text{CH}$ gives predominantly 3- CH_3 -nido-2,3,4,5- $\text{C}_4\text{B}_2\text{H}_5$ with less 2- CH_3 -nido-2,3,4,5- $\text{C}_4\text{B}_2\text{H}_5$, whereas a similar reaction using $\text{CH}_3\text{C}\equiv\text{CCH}_3$ produces 2,3- $(\text{CH}_3)_2\text{C}_4\text{B}_2\text{H}_4$ with less 3,4- $(\text{CH}_3)_2\text{C}_4\text{B}_2\text{H}_4$. Thus the primary insertion occurs at the C—B bonds without C—C cleavage^{9,10}.

The preferred preparation of the nido-carborane 2,3- $\text{C}_2\text{B}_4\text{H}_8$ is effected from pentaborane(9) with acetylene at ca. 200°C or in the presence of base catalyst, such as 2,6-Me₂PY at RT:



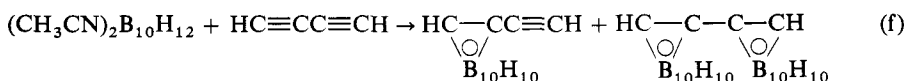
Below RT, Et_3N is utilized in place of 2,6- Me_2py in the preparation of C-substituted nido-2,3- $\text{C}_2\text{B}_4\text{H}_8$ derivatives from appropriately substituted alkynes. Combining this method with the known synthesis of B_5H_9 from $[\text{B}_3\text{H}_8]^-$ salts provides^{13–15} $\text{C}_2\text{B}_4\text{H}_8$ derivatives without the isolation or handling of the air-sensitive B_5H_9 .

An efficient preparation of the icosahedral carborane closo-1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ employs an alkyne with $(\text{Et}_2\text{S})_2\text{B}_{10}\text{H}_{12}$:



The latter complex is the product of Et_2S with $\text{B}_{10}\text{H}_{14}$. Other electron-pair donors, L, particularly aliphatic nitriles and other dialkylsulfides, can be substituted for Et_2S . It is not necessary to isolate the $\text{L}_2\text{B}_{10}\text{H}_{12}$ intermediate, and the alkyne is reacted¹⁶ directly with a solution containing the donor base and $\text{B}_{10}\text{H}_{14}$. From kinetic studies the rate-determining step for the formation¹⁵ of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ from $(\text{Me}_2\text{S})_2\text{B}_{10}\text{H}_{12}$ and various monosubstituted acetylenes involves the attack of the acetylene on the monosulfide, $(\text{Me}_2\text{S})\text{B}_{10}\text{H}_{12}$.

The use of substituted acetylenes, $\text{RC}\equiv\text{CH}$ and $\text{RC}\equiv\text{CR}'$, results in C-substituted 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ derivatives with, e.g., R = ester, amine, amide, acyl halide, halogen, ether, alkyl, aryl, alkenyl or alkynyl¹⁶, although a dialkyne will lead to some bis-carborane¹⁸:



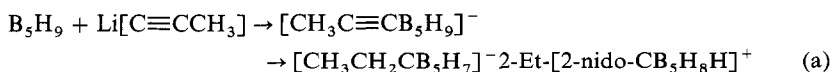
The tetracarbon carborane, $\text{R}_4\text{C}_4\text{B}_4\text{H}_4$, R = CH_3 , C_6H_5 , is obtained from the photolysis (360 nm) of $(\text{OC})_3\text{FeB}_4\text{H}_8$ in the presence of the appropriate alkyne, $\text{RC}\equiv\text{CR}$. There is also mass spectroscopic evidence for the formation of the six- and eight-carbon carboranes, $(\text{CH}_3)_6\text{C}_6\text{B}_4\text{H}_4$ and $(\text{CH}_3)_8\text{C}_8\text{B}_4\text{H}_4$, respectively, in the 2-butyne reaction¹⁹.

The $\text{B}_9\text{H}_{10}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ adduct reacts with acetylene to form²⁰ nido-5,6- $\text{C}_2\text{B}_8\text{H}_{12}$. Reaction of B_5H_9 with alkynes in the presence of thermally generated iron atoms yields as the major product the ferracarborane sandwich complex,²¹ 1-[$\text{h}^6\text{-C}_6\text{Me}_6$]Fe-2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_4$. The carborane nido-2,3-(C_2H_5) $_2\text{C}_2\text{B}_4\text{H}_6$ reacts with 2-butyne in the presence of NaH and NiCl_2 to give a two-carbon insertion into the cage system to produce²² the tetracarbon carborane, nido-4,5,7,8- $\text{Me}_2\text{Et}_2\text{C}_4\text{B}_4\text{H}_4$.

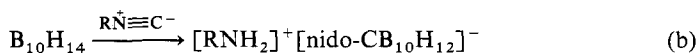
1. T. Onak, in *Boron Hydride Chemistry*, E. L. Muetterties, ed., Academic Press, New York, 1975, p. 349.
2. J. F. Ditter, E. B. Klusmann, J. D. Oakes, R. E. Williams, *Inorg. Chem.*, **9**, 889 (1970).
3. R. R. Rietz, R. Schaeffer, *J. Am. Chem. Soc.*, **95**, 6254 (1973).
4. R. R. Rietz, R. Schaeffer, E. Walter, *J. Organomet. Chem.*, **63**, 1 (1973).
5. R. E. Williams, F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).
6. R. N. Grimes, C. L. Bramlett, *J. Am. Chem. Soc.*, **89**, 2557 (1967).
7. D. A. Franz, R. N. Grimes, *J. Am. Chem. Soc.*, **92**, 1438 (1970).
8. R. N. Grimes, C. L. Bramlett, R. L. Vance, *Inorg. Chem.*, **7**, 1066 (1968).
9. D. A. Franz, V. R. Miller, R. N. Grimes, *J. Am. Chem. Soc.*, **94**, 412 (1972).
10. V. R. Miller, R. N. Grimes, *Inorg. Chem.*, **11**, 862 (1972).
11. T. Onak, F. J. Gerhart, R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963).
12. T. Onak, R. E. Williams, H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).
13. N. S. Hosmane, R. N. Grimes, *Inorg. Chem.*, **18**, 3294 (1979).
14. R. B. Maynard, L. Borodinsky, R. N. Grimes, *Inorg. Synth.*, **22**, 211 (1983).
15. R. G. Swisher, E. Sinn, R. N. Grimes, *Organometallics*, **4**, 890 (1985).
16. H. Beall, in *Boron Hydride Chemistry*, E. L. Muetterties, ed., Academic Press, New York, 1975.
17. W. E. Hill, F. A. Johnson, R. W. Novak, *Inorg. Chem.*, **14**, 1244 (1975).
18. T. E. Paxson, K. P. Callahan, M. F. Hawthorne, *Inorg. Chem.*, **12**, 708 (1973).
19. T. P. Fehlner, *J. Am. Chem. Soc.*, **102**, 3424 (1980).
20. S. Lawrence, J. R. Wermer, S. K. Boocock, M. A. Banks, P. C. Keller, S. G. Shore, *Inorg. Chem.*, **25**, 367 (1986).
21. R. P. Micciche, J. J. Briguglio, L. G. Sneddon, *Organometallics*, **3**, 1396 (1984).
22. M. G. L. Mirabelli, L. G. Sneddon, *Organometallics*, **5**, 1510 (1986).

5.3.2.7.4. by Boron Hydrides with Acetylides, Cyanides, or Isocyanides.

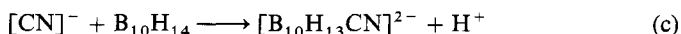
Nucleophilic attack by acetylides, cyanides or isocyanides at a boron site of a polyboron hydride provides a route to C—B bonds. When the propynylide ion is used with pentaborane(9), the 2-ethyl derivative of the monocarborane, 2-CB₅H₉, is realized in low yield through a series of steps that includes internal hydroboration¹:



A zwitterionic [RNH₂]⁺ [CB₁₀H₁₂]⁻ obtained from the action of alkylisocyanides on decaborane(14) is a cage insertion of one carbon atom into a borane hydride framework to give² another compound (as a nitrogen derivative) in the nido-carborane series, CB_nH_{n+4}:



The [B₁₀H₁₃CN]²⁻ anion is prepared³ from decaborane(14) with aq NaCN:



The bis(ethylisocyanide)decaborane, (C₂H₅NC)₂B₁₀H₁₂, is produced from (Et₂S)₂B₁₀H₁₂ with ethylisocyanide²; and the cyano derivatives of [B₁₀H₁₀]²⁻, [Cl_x(NC)_{10-x}B₁₀]²⁻, X = 7-9, are formed upon UV irradiation of Cs₂B₁₀Cl₁₀ and KCN in H₂O. Related chemistry is also effected⁴ with halogen derivatives of [B₁₂H₁₂]²⁻.

A zwitterion carborane, [C₆H₁₁NH₂]⁺ [nido-CB₁₈H₂₀]⁻, is produced from i-B₁₈H₂₂ and cyclohexylisocyanide⁵.

5.3. Formation of Bonds

123

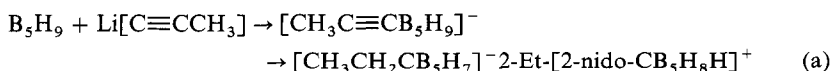
5.3.2. Formation of Carbon—Boron Bonds

5.3.2.7. from Larger Boranes and Carboranes

1. T. Onak, in *Boron Hydride Chemistry*, E. L. Muetterties, ed., Academic Press, New York, 1975, p. 349.
2. J. F. Ditter, E. B. Klusmann, J. D. Oakes, R. E. Williams, *Inorg. Chem.*, **9**, 889 (1970).
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5.3.2.7.4. by Boron Hydrides with Acetylides, Cyanides, or Isocyanides.

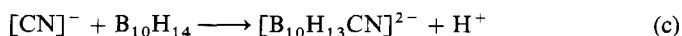
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The [B₁₀H₁₃CN]^{2−} anion is prepared³ from decaborane(14) with aq NaCN:



The bis(ethylisocyanide)decaborane, (C₂H₅NC)₂B₁₀H₁₂, is produced from (Et₂S)₂B₁₀H₁₂ with ethylisocyanide²; and the cyano derivatives of [B₁₀H₁₀]^{2−}, [Cl_x(NC)_{10−x}B₁₀]^{2−}, X = 7–9, are formed upon UV irradiation of Cs₂B₁₀Cl₁₀ and KCN in H₂O. Related chemistry is also effected⁴ with halogen derivatives of [B₁₂H₁₂]^{2−}.

A zwitterion carborane, [C₆H₁₁NH₂]⁺ [nido-CB₁₈H₂₀][−], is produced from i-B₁₈H₂₂ and cyclohexylisocyanide⁵.

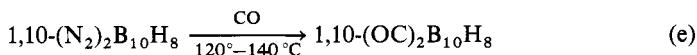
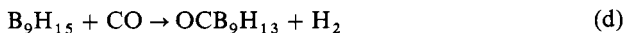
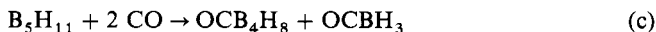
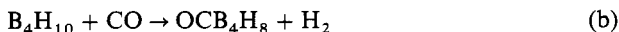
With NaCN, B₅H₉ produces⁶ Na[B₅H₉CN].

(T. ONAK)

1. T. Onak, P. Mattschei, E. Groszek, *J. Chem. Soc., A*, 1990(1969).
2. D. E. Hyatt, D. A. Owen, L. J. Todd, *Inorg. Chem.*, **5**, 1749 (1966).
3. E. L. Muetterties, W. H. Knöth, *Polyhedral Boranes*, Marcel Dekker, New York, 1968.
4. S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1899 (1966).
5. R. I. Sneath, L. J. Todd, *Inorg. Chem.*, **12**, 44 (1973).
6. J. G. Taylor, M. G. H. Wallbridge, *Polyhedron*, **4**, 321 (1985).

5.3.2.7.5. by CO Displacements from Polyboranes.

Polyborane carbonyls with B—C attachments are prepared by displacement^{1–6}:



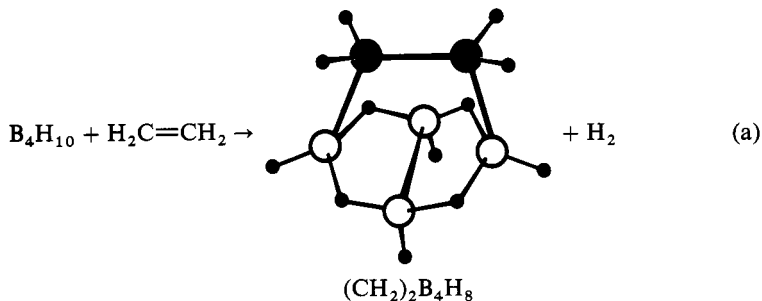
If Eq. (e) is run in the presence of cyclohexane, C₆H₁₁B₁₀H₇(CO)₂ and (C₆H₁₁)₂B₁₀H₆(CO)₂ are formed, suggesting a free-radical mechanism. Whereas the (OC)₂B₁₀H₈ from the bisdiazonium salt is apically substituted only, the monocarbonylation of [1-Me₂S-B₁₀H₉][−] or [2-Me₃N-B₁₀H₉][−] with oxalyl chloride yields the equatorially substituted products 1,6-Me₂SB₁₀H₈CO and (COCl)₂, 2,4- and 2,7(8)-Me₃NB₁₀H₈CO, respectively. Both 1,12- and 1,7-(OC)₂B₁₂H₁₀, as well as [B₁₂H₁₁CO][−], are products of the carbonylation⁵ of hydrated (H₃O)₂B₁₂H₁₂.

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5.3.2.7.6. by Other Reactions Using Polyboranes.

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5.3. Formation of Bonds

5.3.2. Formation of Carbon—Boron Bonds

5.3.2.7. from Larger Boranes and Carboranes

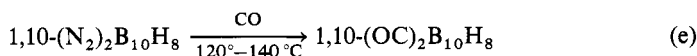
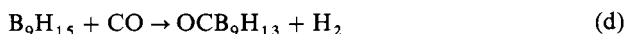
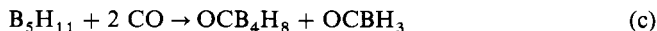
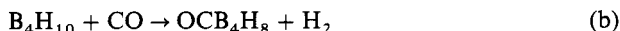
With NaCN, B₅H₉ produces⁶ Na[B₅H₉CN].

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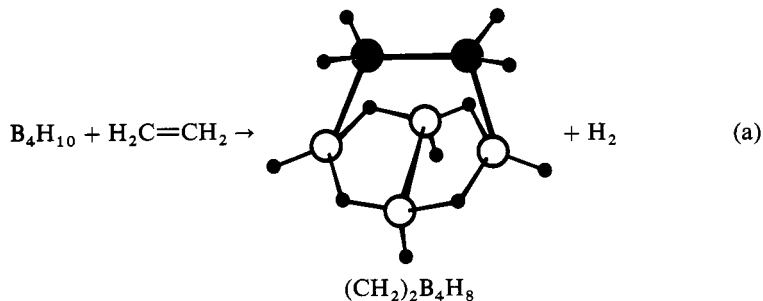
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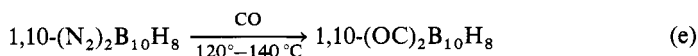
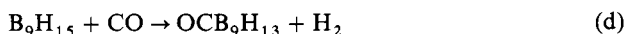
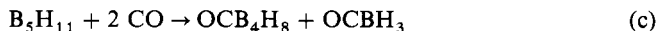
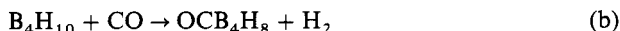
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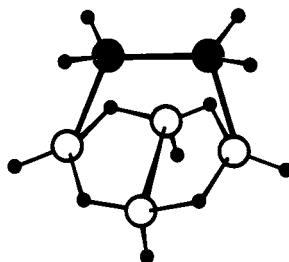
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(CH₂)₂B₄H₈

The methyltetraaborane, $2\text{-CH}_3\text{B}_4\text{H}_9$, is the primary product² of a metal-metal exchange between $(\text{CH}_3)_2\text{Hg}$ and B_4H_{10} .

The only example of a B-aryl derivative of a small carborane is the preparation of $4\text{-C}_6\text{H}_5\text{-2,3-(CH}_3)_2\text{-nido-2,3-C}_2\text{B}_4\text{H}_5$ by an oxidative addition of benzene to the coupled carborane³, $5,5'\text{-}[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2$.

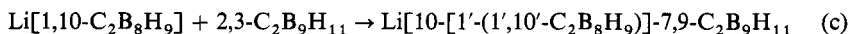
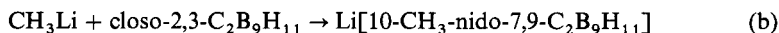
With AlCl_3 , both 1- and 2- $[(\text{ClCH}_2)(\text{CH}_3)_2\text{Si}]\text{B}_5\text{H}_8$ undergo a 1,2- shift of the polyboron cage from Si to the methylene carbon atom to give 1- and 2- $[\text{Cl}(\text{CH}_3)_2\text{SiCH}_2]\text{B}_5\text{H}_8$, respectively, in which the position of the boron attachment at the polyboron cage site is unchanged⁴. Similarly, 1,2-shift of the carboranyl unit of 4- $[\text{ClCH}_2\text{Si}(\text{CH}_3)_2]\text{-nido-2,4-C}_2\text{B}_4\text{H}_7$ from the Si to the methylene carbon is catalyzed by AlCl_3 to yield⁵ 4- $(\text{ClMe}_2\text{SiCH}_2)\text{-nido-C}_2\text{B}_4\text{H}_7$. These same two rearrangements^{4,5} are also thermally encouraged (without a catalyst) at $100\text{--}150^\circ\text{C}$.

By way of a C-insertion process, 1,2-bis(trimethylsilyl)pentaborane(9) gives, on flash thermolysis, a number of C-silyl derivatives of the smallest closo-carborane, i.e., 1- $\text{H}_3\text{Si-1,5-C}_2\text{B}_3\text{H}_4$, 1- $\text{MeH}_2\text{Si-1,5-C}_2\text{B}_3\text{H}_4$ and 2- $\text{Me-1-(H}_3\text{Si)-1,5-C}_2\text{B}_3\text{H}_3$, as well as an equilibrium mixture of 2- and 4-methyl derivatives of closo- CB_5H_7 . The 6-methyl derivative of CB_5H_7 , also formed in small quantities⁶, is the primary carborane product from the pyrolysis⁷ of 2- $(\text{Me}_3\text{Si})\text{-}\mu\text{-(Me}_2\text{B)-B}_5\text{H}_7$.

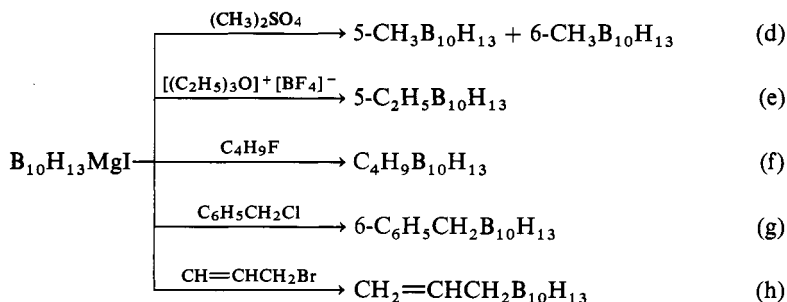
The apically substituted monomethyl derivative of B_5H_9 is a product of dimethyl ether cleavage⁸ by 1- BrB_5H_8 .

The reduced-T reaction of MB_5H_8 ($\text{M} = \text{K}, \text{Li}$) with RX ($\text{X} = \text{Br}, \text{I}$) forms 2- $\text{R-B}_5\text{H}_8$ ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2\text{-}, \text{CH}_2=\text{CH-CH}_2\text{-}$)⁹. Alkylation of $[\text{7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ with RX ($\text{X} = \text{halogen}$) below 0°C in H_2O , alcohol or tetrahydrofuran (THF) yields $[\text{11-R-2,7-nido-C}_2\text{B}_9\text{H}_{11}]^-$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{CH}_2=\text{CHCH}_2$) but at RT $[\text{8-R-7,9-nido-C}_2\text{B}_9\text{H}_{11}]^-$ is found along with B-mono, di and trialkyl derivatives; benzylation of $[\text{7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ in liq NH_3 produces¹⁰⁻¹¹ $[\text{9-C}_6\text{H}_5\text{CH}_2\text{-7,8-C}_2\text{B}_9\text{H}_{11}]^-$. Acylation of both the 7,8- and $[\text{7,9-C}_2\text{B}_9\text{H}_{12}]^-$ anions results in B-acyl derivatives of this nido-carborane system¹².

The action of carbanionic nucleophiles on closo- $2,3\text{-C}_2\text{B}_9\text{H}_{11}$, give rise to boron-attached moieties¹³:

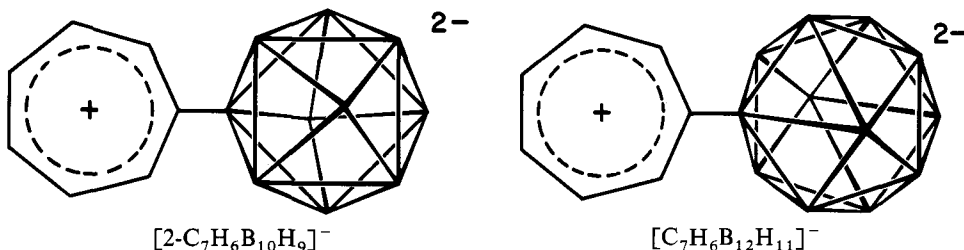


Similarly, methyl lithium reacts with $\text{B}_{10}\text{H}_{14}$ to yield primarily 6-(and 9)-methyl-substituted derivatives of this 10-boron polyborane. Organomagnesium-halide reagents also produce the 6-alkylated decaboranes, but in low yield; the major product is $\text{XMgB}_{10}\text{H}_{13}$. The latter, as also does $[\text{B}_{10}\text{H}_{13}]^-$ anion, reacts¹⁴ with organic reagents to form $\text{RB}_{10}\text{H}_{13}$:

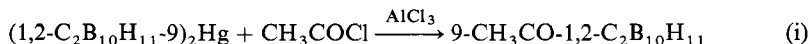


Arylmagnesium halides and aryllithiums afford the dianions of B-aryldicarbaboradodecaborates(14) with $[1,2-C_2B_{10}H_{12}]^{2-}$. These, on oxidation with $CuCl_2$, yield a mixture of 3-, 4-, 8- and 9-aryl-closo-1,2- $C_2B_{10}H_{11}$ (aryl = C_6H_5 , m- and p- FC_6H_4 , m- and p- $CH_3C_6H_4$). Similarly, 1,12- $C_2B_{10}H_{12}$ yields a mixture of B-aryl derivatives of the cage-rearranged 1,7- $C_2B_{10}H_{12}$. Other B-substituted derivatives of the type B-R-1,2- $C_2B_{10}H_{11}$ (R = CH_3 , C_4H_9 , $CH=CH_2$, $CH=CHC_6H_5$) are also prepared from $[1,2-C_2B_{10}H_{12}]^{2-}$ with organolithium or $RMgX$ reagents followed by treatment¹⁴⁻¹⁶ with $CuCl_2$.

Tropenylum ion reacts with either $[B_{10}H_{10}]^{2-}$ or $[B_{12}H_{12}]^{2-}$ ions to yield $[2-C_7H_6B_{10}H_9]^-$ and $[C_7H_6B_{12}H_{11}]^-$, respectively^{18,19}:



The 2-benzoyl derivative of $[B_{10}H_{10}]^{2-}$ ion is obtained from acylation¹⁹ of this ion with C_6H_5COCl . A-B-acetyl derivative of closo-1,2- $C_2B_{10}H_{12}$ is formed from $AlCl_3$ -catalyzed acetylation²¹ of $(1,2-C_2B_{10}H_{11}-9)_2Hg$:



Introduction of a phenyl group onto a 10-B polyborane is accomplished in one instance by the decomposition²² of $(C_6H_5)_2SnB_{10}H_{13}$ at $95^\circ C$ to yield 6- $H_6C_5-B_{10}H_{13}$. Thermal decomposition of $[(C_2H_5)_3NH]_2B_{10}Br_{10}$ near $430^\circ C$ produces $C_2H_5B_9Br_8$, $CH_3B_9Br_8$, $(CH_3)_2B_9Br_7$ and $C_2H_5(CH_3)B_9Br_7$ in low yield²³. Benzene with 1,7- $C_2B_{10}H_{12}$ at 630° – $750^\circ C$ yields a mixture of B- C_6H_5 -1,7- $C_2B_{10}H_{11}$ isomers²⁴. Heating 1,2- $C_2B_{10}H_{12}$ with C_6F_6 at $500^\circ C$ gives²⁵ B-pentafluorophenyl isomers of both 1,2- and 1,7- $C_2B_{10}H_{12}$.

From 9-vinyl- and 9-ethynyl-derivatives of 1,2- and 1,7- $C_2B_{10}H_{12}$ are prepared from 9- IMg -1,2-(or 1,7-)- $C_2B_{10}H_{11}$ with vinyl or alkynyl halides in the presence of $[(C_6H_5)_3]_4Pd$; a 9-vinyl derivative is also produced from $C_6H_5C\equiv CH$ and 9- $(CF_3)_3CO_2$ -2,11-1,2- $C_2B_{10}H_{11}$ in the presence of $Pd(OCOCH_3)_2$; the 9-alkyl and 9-phenyl derivatives are formed from 9-Br- (or I-) 1,2-(or 1,7-)- $C_2B_{10}H_{11}$ and $RMgX$ (R = alkyl, phenyl, X = halogen) in the presence of similar Pd catalysts. Analogous chemistry is known for the 1,12- $C_2B_{10}H_{12}$ system²⁶⁻³³.

The iminium salt $[Me_2N=CH_2]I$ with $[B_5H_8]^-$ produces $\mu-(Me_2NCH_2)B_5H_8$ in which a bridging H atom of B_5H_9 is replaced by a C-N two-atom bridge, the Me_2NCH_2 group³⁴. Pentaborane(9) is stereospecifically tris-alkylated with $LiEt_3BH$ to give 2,3,4-triethylpentaborane(9), whereas use of $Li(EtCHMe)_3BH$ results only in the monoalkyl product, 2-sec-butylpentaborane(9). A mechanism is proposed involving addition of $[Et_3BH]^-$ to the base of the B_5H_9 pyramid to form an intermediate, $[Et_3B_6H_{10}]^-$, followed by Et-group migration to adjacent boron atoms to relieve steric strain³⁵. Pentaborane(9) with ethylene, propylene, and 1-butene, etc., in the presence of $PdBr_2$,

gives excellent yields of 1- and 2-substituted alkenylpentaboranes under mild conditions³⁶. The B—B bond of 1-(Cl₂B)B₃H₈ inserts C₂H₄ at RT to form³⁷ 1-[2-(dichloroboryl)ethyl]pentaborane(9). The AlCl₃-catalyzed substitution of 2-ClB₅H₈ with alkylbenzenes give 2-RB₅H₈ (R = Ph, tolyl, xylyl, C₆H₂Me₃)³⁸.

The reaction of B₄Cl₄ with Me₃CLi gives³⁹ (Me₃C)₄B₄.

Carboethoxycarbene, :CHCO₂Et, with 1,2-C₂B₁₀H₁₂ forms all four possible products of B—H insertion, X-EtOCOCH₂-1,2-C₂B₁₀H₁₁ (X = 3, 4, 8, and 9)⁴⁰.

(T. ONAK)

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36. T. Davan, E. W. Corcoran, L. G. Sneddon, *Organometallics*, **2**, 1693 (1983).
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5.3.3. Formation of Carbon—Al Bonds

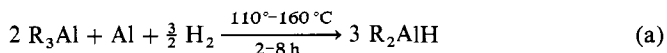
5.3.3.1. from the Elements.

This topic is presented in §5.10.2.

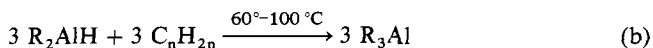
5.3.3.2. from Al Metal and Its Alloys

5.3.3.2.1. by the Interaction of H₂, Olefin and Aluminum Metal.

The direct synthesis of organoaluminums¹⁻⁵ is of industrial importance because of the application of these compounds in heterogeneous and homogeneous catalysis^{6,7}. The direct synthesis works because activated Al metal reacts¹⁻⁵ in an autoclave with dry H₂ [5×10^6 – 3×10^7 pa (50–300 atm)] in the presence of R₃Al (neglecting association):



The R₂AlH are formed in high yield and react with terminal olefins [e.g., C₂H₄, C₃H₆, CH₂=CHCH₂CH₃, CH₂=C(CH₃)₂ and R=Et, n-Pr, n-Bu, and i-Bu, etc.] at several atm of the acetylene-free olefine to give R₃Al (see also §5.3.3.4.1):



The overall reaction is then represented by:



and the growth factor of R₃Al is 1.5.

Prolonged ball milling (ca. 12 h) of commercial Al powder in a sulfur-free hydrocarbon together with the AlR₃ required to prevent further oxidation of the Al yields finely divided metal in a reactive state^{1,5,8}. The suspension may be used directly in Eq. (a). Other metals, either as impurities or as an alloy with the Al ($\leq 1\%$ V, Nb, Ta, U, Sc, Zr, Hf or especially Ti), accelerate reaction (a)^{1-5,8,9}. This is also claimed for Al–Si alloys (13–40% Si), which are brittle and can be powdered^{10,11}. Contamination of the Al metal with Fe, Ni, Cu, Li, Sn and in particular Pb is disadvantageous. An increase in the Ti content compensates for these unfavorable effects¹.

The differing conditons for reactions (a) and (b) indicate that the choice for a one-step or a two-step synthesis is determined by the thermal stability or chemical reactivity

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5.3.3. Formation of Carbon—Al Bonds

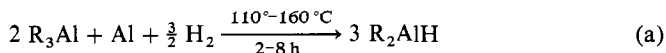
5.3.3.1. from the Elements.

This topic is presented in §5.10.2.

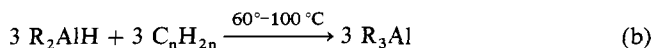
5.3.3.2. from Al Metal and Its Alloys

5.3.3.2.1. by the Interaction of H₂, Olefin and Aluminum Metal.

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The R₂AlH are formed in high yield and react with terminal olefins [e.g., C₂H₄, C₃H₆, CH₂=CHCH₂CH₃, CH₂=C(CH₃)₂ and R=Et, n-Pr, n-Bu, and i-Bu, etc.] at several atm of the acetylene-free olefine to give R₃Al (see also §5.3.3.4.1):



The overall reaction is then represented by:

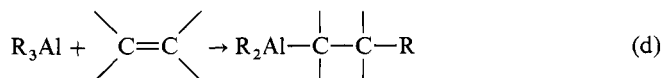


and the growth factor of R₃Al is 1.5.

Prolonged ball milling (ca. 12 h) of commercial Al powder in a sulfur-free hydrocarbon together with the AlR₃ required to prevent further oxidation of the Al yields finely divided metal in a reactive state^{1,5,8}. The suspension may be used directly in Eq. (a). Other metals, either as impurities or as an alloy with the Al ($\leq 1\%$ V, Nb, Ta, U, Sc, Zr, Hf or especially Ti), accelerate reaction (a)^{1-5,8,9}. This is also claimed for Al-Si alloys (13–40% Si), which are brittle and can be powdered^{10,11}. Contamination of the Al metal with Fe, Ni, Cu, Li, Sn and in particular Pb is disadvantageous. An increase in the Ti content compensates for these unfavorable effects¹.

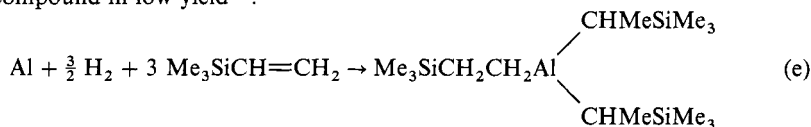
The differing conditions for reactions (a) and (b) indicate that the choice for a one-step or a two-step synthesis is determined by the thermal stability or chemical reactivity

of the final product, AlR₃. Therefore, the reverse of reaction (b), dehydroalumination, as well as the repeated addition of R₃Al to olefin:



must be considered (see also §5.3.3.5.1): Because the reactivity of olefins toward R₃Al is sharply reduced in the series H₂C=CH₂ > H₂C=CHR > H₂C=CRR', reaction (d) is a serious problem in the synthesis of Et₃Al, but it is less important for longer R chains and it is of no importance for 1,1-dialkylethylenes leading^{1,5,12}, e.g., to (i-C₄H₉)₃Bu.

For triethylaluminum, the two-step synthesis [Eqs. (a) and (b)] is essential; it is also recommended for tripropylaluminum and should be used if pure R₃Al compounds are required^{1,5}. Reactions (a) and (b) are regiospecific for terminal olefins, leading almost exclusively to the n-alkyls. However, with styrene or with trialkylvinylsilane, mixtures are observed (see also §5.3.3.4.1). The reaction of Al, H₂ and trimethylvinylsilane gives the RAlR'₂ compound in low yield¹³:



The equilibrium in Eq. (b) is shifted to the left at elevated T, and a significant amount of dialkylaluminum hydride and free olefin is present when the alkyl group is branched at the β position (e.g., in i-Bu₃Al)^{5,14}.

Nonterminal olefins are used in the direct synthesis, and R₂AlH compounds (R = s-alkyl- or cyclo-alkyl) are obtained according to Eq. (a)¹⁵. The conditions (120°–130°C, 20 h) are more drastic than for terminal olefins.

Isomerization of di-s-alkylaluminum hydrides to other s-alkyl compounds or even to n-alkylaluminums may occur^{1,13} (see also §5.3.3.4.2 and §5.3.3.5.3) depending on the structure of the nonterminal olefin.

The direct synthesis of organoaluminums is powerful, well-developed and perfected for Et₃Al, n-Pr₃Al, i-Bu₃Al, Et₂AlH or i-BuAlH. Because these products are now prepared on an industrial scale, their laboratory synthesis is of minor importance. The direct synthesis opens an economical route to exploiting the enormous versatility of the Al—C and Al—H bonds in synthesis.

(B. WRACKMEYER)

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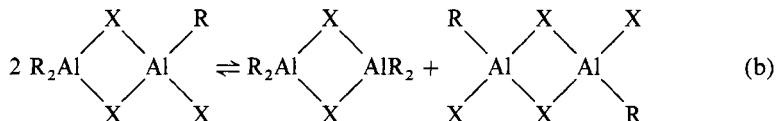
5.3.3.2.2. by the Action of Organic Halides on Aluminum.

The action of organic halides on Al metal and its alloys is the subject of many patents. Except for the behavior of methyl-, ethyl- and some aryl halides there is poor agreement concerning experimental procedures, reproducibility and yields¹⁻³.

The reaction between an organic halide and Al yields the organoaluminum sesquichloride, $R_3Al_2X_3$:



which is not a single compound but in equilibrium with dimeric diorganoaluminum halide and dimeric organoaluminum dihalide^{4,5}:

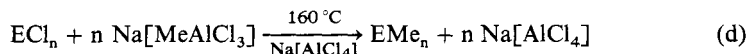
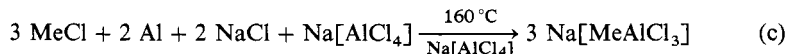


The conditions for reaction (a) vary with R and X, and the yields depend on the state of the Al metal.

Methyl and ethyl iodide react at 40°C and 70°C to yield liquids of composition $Me_3Al_2I_3$ and $Et_3Al_2I_3$, respectively, which on distillation give redistribution products (see §5.3.3.3.2) depending on conditions^{6,7}. With alkyl iodides it is possible to prepare the sesquiiodides $R_3Al_2I_3$ with longer R chains (e.g., R = n-Bu, n-Oct)¹. Aluminum reacts with iodobenzene or with p-iodotoluene in 40 h at 100°C to the arylaluminum sesquiodides⁸. Aluminum metal ball milled with $AlCl_3$ reacts¹ with iodobenzene at RT. Any activation of the Al helps to start the reaction more smoothly. A small amount of previously prepared organoaluminum halide, or AlX_3 , prepared in situ by addition of a few crystals of I_2 or a small portion of Br_2 is effective. Likewise, the precipitate of finely divided Al metal that is obtained from the reduction of organoaluminum sesquihalides with sodium can be used⁹ (see §5.3.3.3.4).

Activation of the Al metal is essential for the reaction with organic chlorides and bromides. These reactions are unimportant industrially as compared with the advantage of the direct synthesis (see §5.3.3.2.1) followed by redistributions with AlX_3 (see §5.3.3.3.2); but they are important in the laboratory. The preparation of the methyl- and ethylaluminum sesquichlorides or -bromides is detailed^{1,3}. However, even following the exact experimental instructions does not insure completely against failure¹. **A potential hazard derives from the slow initiation and highly exothermic reaction.**

The thermal stability of methylaluminums allows the reaction of Al metal in a NaCl- $AlCl_3$ melt at 160°C with methyl chloride to give the complex salt $Na[MeAlCl_3]$. This is a powerful reagent for converting metal halides into their volatile permethylated derivatives (e.g., Me_3B , Me_4Si , Me_4Ge , Me_4Sn)¹⁰:



5.3. Formation of Bonds

5.3.3. Formation of Carbon—Al Bonds

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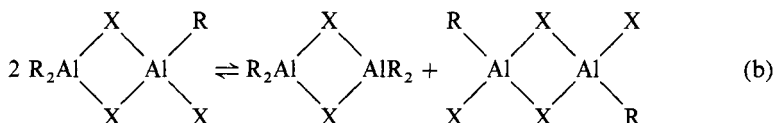
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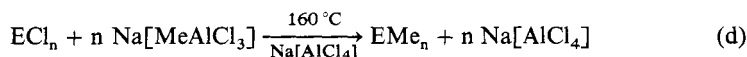
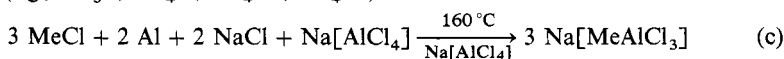


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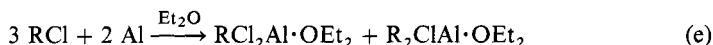
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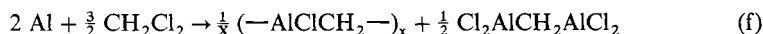
The autocatalytic formation of alkanes, alkenes, polymers, AlX_3 and HX prevents the use of higher alkyl chlorides or bromides for the synthesis of the corresponding sesquihalides in nonetheral solvents^{11,12}. The electron-pair acceptor acid-catalyzed elimination of HX ($\text{X}=\text{Cl}, \text{Br}$) cannot occur with CH_3X and is unimportant for $\text{C}_2\text{H}_5\text{X}$ provided T is as low as possible. To circumvent these problems, alkylaluminum sesquiodides (weaker electron-pair acceptor acids) are used to initiate the reaction and Et_2O is added to form adducts with the alkylaluminum halides¹³:



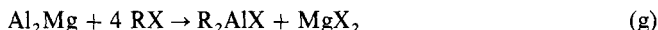
Reaction (e) is also useful for preparing mixtures of ether adducts of allyl-¹⁴⁻¹⁷, crotyl-^{15,17}, propargyl-¹⁴ and benzylaluminum bromides¹⁴. The organo bromides are used to insure enhanced reactivity (as compared with the chlorides) and less coupling (as compared with the iodides).

Excess chloro- and bromobenzene reacts with Al metal activated by ball milling in the presence of AlCl_3 to give $\text{R}_3\text{Al}_2\text{X}_3$. The reaction takes ca. 70 h if the mixture is heated in the ball mill at $\leq 110^\circ\text{C}$ ^{1,18}.

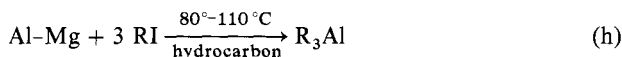
Methylenealuminums are accessible from methylene chloride with Al metals. The reaction is initiated with methylene bromide and finally, after the colorless solid formed during the reaction is extracted with hot CH_2Cl_2 , $\text{Cl}_2\text{AlCH}_2\text{AlCl}_2$ is obtained in 61 % yield^{1,19}. The second product from this reaction is a polymer of the composition¹⁹ $(-\text{AlClCH}_2-)_x$:



The use of Al-Mg alloys for the preparation of organoaluminums is of interest because the amount of Mg may determine the composition of the organoaluminum (e.g., for a 70:30 Al-Mg alloy):



Activation of the alloy is again important. However, the reactions are nonstoichiometric. Ether adducts of R_3Al are formed using alkyl bromides and alloys of low Al content (ca. 15 %) in Et_2O ¹. In phenyl ethers (e.g., anisole, phenetole) the R_3Al adducts are less stable to dissociation, which allows isolation of less volatile R_3Al [e.g., $(\text{n-C}_6\text{H}_{13})_3\text{Al}$]^{20,21}. These reactions can be carried out with Al-Mg alloy or with a mixture of Al and Mg powder. These mixtures act, e.g., in the formation of the Si—Al bond (see §5.3.8). In hydrocarbons the R_3Al ($\text{R} = \text{n-C}_5\text{H}_{11}$ to $\text{n-C}_{12}\text{H}_{23}$) can be prepared from alkyl iodides²¹:



Aluminum vapor reacts with $[\text{CF}_3]^\cdot$ radicals to product unstable AlCF_3 compounds²³.

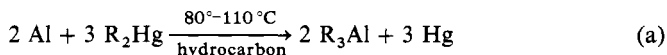
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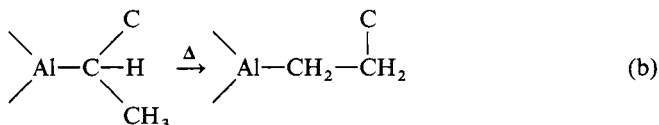
5.3.3.2.3. by the Reaction of Organomercurials with Al.

The synthesis of R_3Al via the historic reaction of R_2Hg (**high toxicity**) with xs Al metal is still useful on a small laboratory scale¹⁻³ ($R = n\text{-alkyl}$):



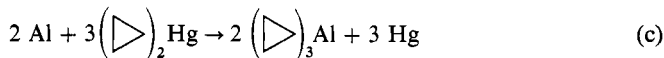
The clean surface of Al foil, wire or turnings is activated by mercury(II) chloride prior to use. The transfer of R groups ($\text{CH}_2\text{—X}$) is straightforward, e.g., with $R = \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ⁴, CH_2Ph ⁵, CH_2SiMe_3 ⁶. Therefore, this can be an attractive method, considering the availability of diakylmercurials⁷⁻⁹ (see also §5.7.2).

Attempts to prepare secondary or tertiary alkylaluminums are only partly successful owing to the instability of these compounds under the reaction conditions ($80^\circ\text{--}100^\circ\text{C}$). Thus reaction (a) for $R = \text{Pr-}i$ gives a mixture⁷ of $n\text{-Pr}_3\text{Al}$ and $i\text{-Pr}_3\text{Al}$, and the same is true for $R = \text{Bu-}s$ leading to $s\text{-Bu}_3\text{Al}$ and mainly¹⁰ to $n\text{-Bu}_3\text{Al}$:



Reduced optical purity owing to racemization is observed for tris(2-methylbutyl)aluminum, which is prepared¹ from optically active bis-2-methylbutylmercury at 110°C .

Dicyclopopylmercury yields tricyclopopylaluminum¹²:



5.3. Formation of Bonds

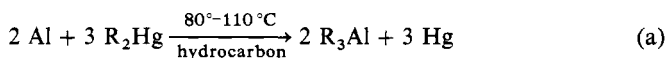
5.3.3. Formation of Carbon—Al Bonds

5.3.3.2. from Al Metal and Its Alloys

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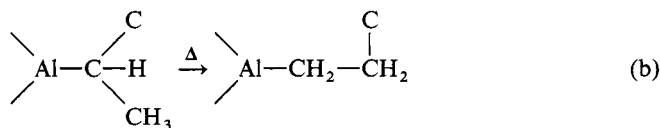
5.3.3.2.3. by the Reaction of Organomercurials with Al.

The synthesis of R_3Al via the historic reaction of R_2Hg (**high toxicity**) with xs Al metal is still useful on a small laboratory scale¹⁻³ ($R = n\text{-alkyl}$):



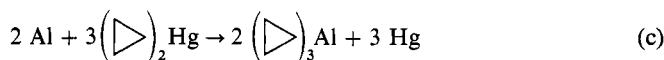
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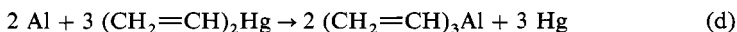


Reduced optical purity owing to racemization is observed for tris(2-methylbutyl)aluminum, which is prepared¹ from optically active bis-2-methylbutylmercury at 110°C .

Dicyclopropylmercury yields tricyclopropylaluminum¹²:

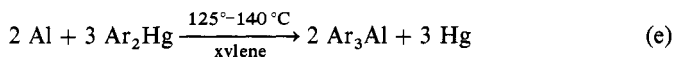


Similarly, trivinylaluminum is prepared via the reaction between divinylmercury and xs Al:



The reaction is conducted in pentane by heating to the bp and cooling to 0°C as soon as the first trace of Hg metal appears¹³. Alternatively, a more polar solvent, CH₂Cl₂, is suggested at -25°C¹⁴. Polymerization of pure trivinylaluminum starts at -10°C, and is complete at 20°C within a few h^{13,14}. The (CH₂=CH)₃Al·D adducts [D = Et₂O, tetrahydrofuran (THF), Me₃N, C₅H₅N] are thermally more stable and can be distilled in vacuo without decomposition¹³. Trialkyn-1-ylaluminum etherates, (RC≡C)₃Al·D, are obtained in 60–80% yield from the reaction between finely divided Al and dialkyn-1-ylmercury in ethers¹⁵ (D = Et₂O, THF; R = alkyl, phenyl). The ether is displaced by tertiary amines or pyridine¹⁵. The uncomplexed trialkyn-1-ylaluminums polymerize more readily than trivinylaluminum.

Triarylaluminums can be prepared via the reaction between Al metal and the diarylmercurial^{16–18}:



A high-bp hydrocarbon is used as a solvent in order to prevent local overheating and decomposition of the arylaluminums. Reaction (e) tolerates substituents on the aromatic rings (e.g., 4-F, 4-Cl, 2-MeO, 2-Me, 3-Me, 4-Me). However, there are Ar₂Hg compounds that do not react [e.g., Ar = 4-MeO-C₆H₄, 4-EtOC₆H₄, 4-C₂H₅OC(O)C₆H₄, 2-MeOC(O)C₆H₄], and there are some that react with Al metal to give undefined decomposition products (e.g., Ar = 2-Cl, 2-EtOC₆H₄, 2-naphthyl).

The sometimes drastic conditions required to complete the reactions between Al metal and diorganomercurials together with the limited thermal stability of many organoaluminums confine this reaction to specific examples.

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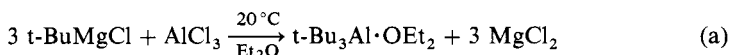
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5.3.3.3. from Al Halides or Organoaluminum Halides

5.3.3.3.1. by Reaction with Polar Organometallics.

Metal-metal exchange is a convenient method to C—Al bonds. Organoalkali, e.g., RLi, RNa, and R_2Mg , RMgX, reagents react with AlX_3 (e.g., $AlCl_3$, $AlBr_3$) or organoaluminum halides, (e.g., $R'AlX_2$, $R''AlX$; $X = Cl, Br$), to give the desired products. By these reactions any C—Al bond can be formed (e.g., Al-alkyl, -allyl, -alkenyl, -aryl, -alkynyl)¹⁻³.

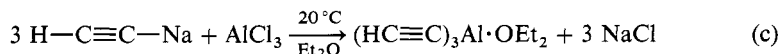
In the syntheses of trialkylaluminums, primary, secondary or tertiary alkyl groups are transferred from Li or Mg to Al; e.g., $t\text{-Bu}_3Al \cdot OEt_2$ is isolated as a crystalline solid in >70% yield⁴ ($AlCl_3$ in Et_2O is added to the organomagnesium-halide reagent):



The ether-free $t\text{-Bu}_3Al$ is obtained from the analogous reaction between $t\text{-BuLi}$ and $AlCl_3$ in pentane⁴. Using ether-free RMgX reagents⁵ with R_2AlCl gives R_3Al in high yield⁵. However, an efficient method for removing the ether via a fluoride complex is available⁶:



Triorganoaluminums with unsaturated C—C bonds adjacent to Al can be prepared from the respective organolithium, -sodium or -magnesium halide reagents. However, the solvate-free compounds ($R = \text{alkenyl, alkynyl}$) are unstable and, therefore, should be isolated as ether adducts^{1,5}:



The $HC \equiv CNa$ is suspended in ether and ground in a ball mill before the ethereal solution of $AlCl_3$ is added. The crystalline product is obtained in 90% yield¹. **Caution:** The etherates $(HC \equiv C)_3Al \cdot OR_2$ should not be sublimed, because free $(HC \equiv C)_3Al$ may detonate at elevated T.

The $R_2AlC \equiv C-R'$ compounds are prepared from $R'C \equiv CLi$, $R'C \equiv CNa$ or $R'C \equiv CMgCl$ with or without ether by reaction with the diorganoaluminum halide^{1,7}. Ether complexes of $R_2AlC \equiv CR'$ are weak, and the dimeric compounds are stable toward disproportionation which otherwise is common to R_2AlR' compounds⁸.

Triphenylaluminum etherate can be prepared from $PhMgX$ ($X = Cl, Br$)⁹ in 50–75% yield, although this is not a convenient procedure (see §5.3.3.4). In contrast to trialkylaluminums, the ether can be removed by heating the adduct in vacuo. Pure Ph_3Al is also obtained from the reaction of ether-free $PhMgBr$ with $AlCl_3$ in dodecane in 75% yield after recrystallization from xylene¹⁰.

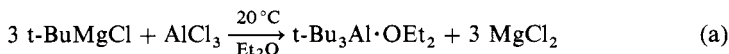
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5.3.3.3. from Al Halides or Organoaluminum Halides

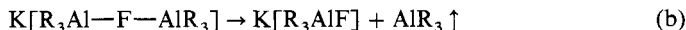
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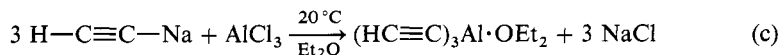
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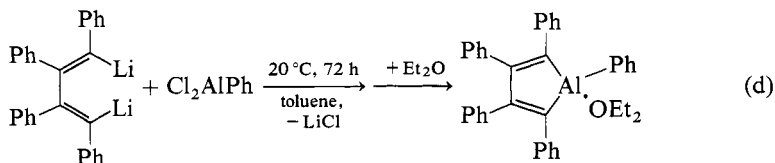


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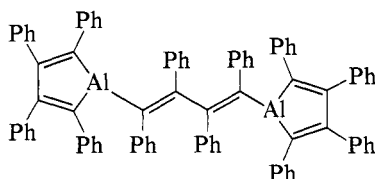
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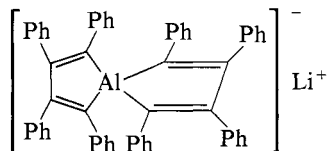
Although many R_2AlR' compounds exist in equilibrium with R_3Al and R'_3Al , cyclic compounds are stable. A pentaphenylaluminacyclopentadiene is known as the etherate (67% yield)¹¹:



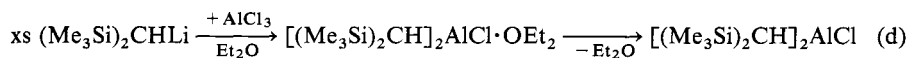
The same reaction (3:2 stoichiometry) with $AlCl_3$ in toluene yields a 1,4-bis-alumina-structure:



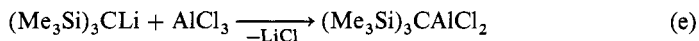
whereas in Et_2O (2:1 stoichiometry) intramolecular ionic complex formation takes place to give a spiro compound¹²:



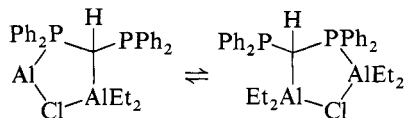
The reaction of organometallics with aluminum trihalides in a 2:1 stoichiometry leads to R_2AlX . A 1:1 stoichiometry gives $M[RAiX_3]$ rather than $RAiX_2$. Adducts are obtained in the presence of ether. Complex formation is reversible only for weak bases such as phenyl ethers. Otherwise, ether cleavage may occur when the etherates are heated at $>100^\circ\text{C}$. However, with bulky organo groups the ether may be removed in vacuo¹³:



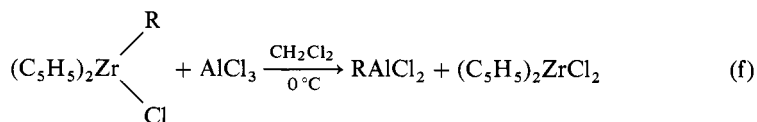
A monomer is obtained in 15% yield when the bulky $(\text{Me}_3\text{Si})_3\text{C}$ group is used¹⁴:



Mono- and diphosphinomethylaluminums¹⁷ result from the Li derivatives and $AlCl_3$, Me_2AlCl or Et_2AlCl , e.g.:



Stereoselective hydrozirconation can be followed by a metal-metal exchange reaction^{14,15}:



Organoaluminum halides are more readily available by other methods, of which the redistribution reaction (see §5.3.3.2) is the most versatile.

(B. WRACKMEYER)

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5.3.3.3.2. by Redistribution with Organoaluminums.

Redistribution between organoaluminums is useful for organoaluminum halides and for triorganoaluminums¹⁻³.

Alkylaluminum dihalides, RAlX_2 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$, are prepared (neglecting association) either by mixing the pure compounds or by conducting the reaction in an inert solvent such as hexane or heptane:



for $\text{X} = \text{Cl}$ long reaction times and heating are required. The exact stoichiometry is important.

Dialkylaluminum halides, R_2AlX , $\text{X} = \text{Cl}, \text{Br}, \text{I}$, are prepared in the same way (neglecting association). For $\text{X} = \text{Cl}$ slight xs of AlCl_3 is used, and the small amount of RAlCl_2 thus formed is trapped by adding NaCl as NaRAlCl_3 :

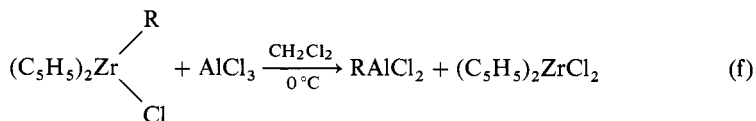


5.3. Formation of Bonds

5.3.3. Formation of Carbon—Al Bonds

5.3.3.3. from Al Halides or Organoaluminum Halides

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18. D. B. Carr, J. Schwartz, *J. Am. Chem. Soc.*, 99, 638 (1977).
19. D. B. Carr, J. Schwartz, *J. Am. Chem. Soc.*, 101, 3521 (1979).

5.3.3.3.2. by Redistribution with Organoaluminums.

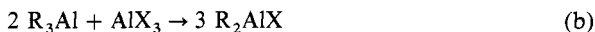
Redistribution between organoaluminums is useful for organoaluminum halides and for triorganoaluminums¹⁻³.

Alkylaluminum dihalides, RAlX_2 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$, are prepared (neglecting association) either by mixing the pure compounds or by conducting the reaction in an inert solvent such as hexane or heptane:



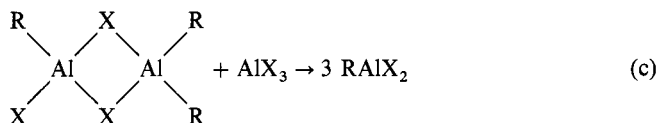
for $\text{X} = \text{Cl}$ long reaction times and heating are required. The exact stoichiometry is important.

Dialkylaluminum halides, R_2AlX , $\text{X} = \text{Cl}, \text{Br}, \text{I}$, are prepared in the same way (neglecting association). For $\text{X} = \text{Cl}$ slight xs of AlCl_3 is used, and the small amount of RAlCl_2 thus formed is trapped by adding NaCl as NaRAlCl_3 :



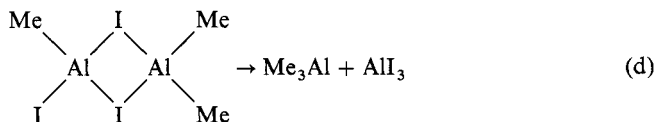
Most alkylaluminum halides are obtained in quantitative yield and are purified by distillation in high vacuum⁴, although this is not necessary. Thermal decomposition of RAlX_2 or R_2AlX may occur at low T^1 [e.g., $(i\text{-Bu})_2\text{AlCl}$, $>75^\circ\text{C}$].

The RAlX_2 , R_2AlX or sesquihalides ($\text{RXAlX}_2\text{AlR}_2$) are available by the reaction of metallic Al with organic halides (RX) (see §5.3.3.2.2.)¹⁻³. Redistributions of these compounds, similar to Eqs. (a) and (b), take place smoothly between the sesquihalides and AlX_3 to give RAlX_2 :



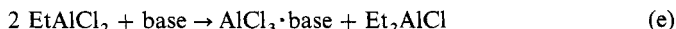
Reactions (a)–(b) are fast. The redistribution process, however, is retarded in the presence of xs base (e.g., ethers or tertiary amines), although the equilibrium still lies on the same side as in Eqs. (a)–(c).

It is not practicable to shift the equilibria in Eqs. (a)–(c) to the left. However, with methylaluminum sesquiodide, it is possible to shift the equilibrium toward Me_3Al by fractional distillation in vacuum (100 torr, $1.33 \times 10^4 \text{ Pa}$)⁵:



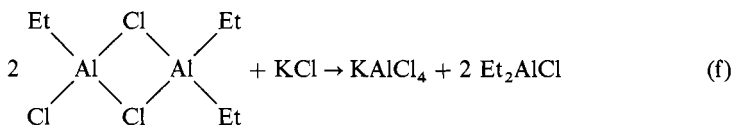
This is a convenient method for Me_3Al in the laboratory. Similarly, Ph_3Al is from $\text{Ph}_3\text{Al}_2\text{Cl}_3$ and Et_3Al by removing Et_2AlCl from the equilibrium and leaving the Ph_3Al behind⁶.

Another method to effect the equilibria in Eqs. (a)–(c) is based upon the differing electron-pair acceptor acidity of the components. The acidity decreases $\text{AlCl}_3 > \text{RAlCl}_2 > \text{R}_2\text{AlCl}$, R_3Al , which means that the addition of a deficit of a base (e.g., Et_2O or pyridine) can influence the equilibria of Eqs. (a)–(c)⁷:



In hydrocarbon solvents the $\text{AlCl}_3 \cdot \text{base}$ complexes precipitate, which makes the isolation of R_2AlCl simple⁸.

Halide ions may also serve as bases that affect the equilibria. Thus, KCl complexes⁹ Et_2AlCl , EtAlCl_2 and AlCl_3 . Owing to the stability and insolubility of KAlCl_4 , the reaction proceeds smoothly to give Et_2AlCl in 97% yield¹⁰:

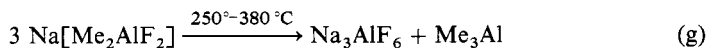


Sodium chloride is not recommended because the decomposition of $\text{Na}[\text{RAlCl}_3]$ requires drastic conditions.

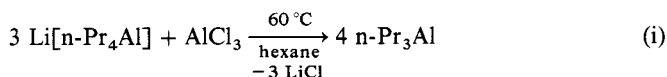
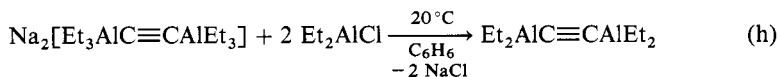
The organoaluminum fluorides can be prepared by Eqs. (a) and (b) ($\text{X} = \text{F}$). However, the use of reactive AlF_3 , as prepared¹¹ from BF_3/AlR_3 , is essential. It is more

convenient to obtain¹¹ R_2AlF from the reaction between R_2AlCl and finely powdered NaF.

Dimethylaluminum fluoride is an intermediate in the preparation of Me_3Al via Me_2AlCl in the presence of NaF. The equilibrium in Eq. (g) is shifted to the right owing to the formation¹¹ of the stable Na_3AlF_6 :



Finally, tetraorganoaluminates react with Al halides to give organoaluminum compounds^{1,2,12}:

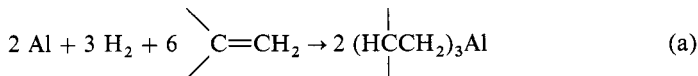


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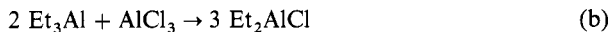
1. H. Lehmkuhl, K. Ziegler, *Aluminium-Organische Verbindungen*, in *Methoden der Organischen Chemie (Houben Weyl)*, E. Müller, ed., Vol. 13/4, Georg Thieme Verlag, Stuttgart, 1970, p. 58.
2. T. Mole, E. A. Jeffrey, *Organoaluminium Compounds*, Elsevier, Amsterdam, 1972.
3. G. Zweifel, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 3, D. ed. Pergamon Press, Oxford, 1979, p. 1013.
4. H. Reinheckel, K. Haage, *J. Prakt. Chem.*, **33**, 70 (1966).
5. K. S. Pitzer, H. S. Gutowsky, *J. Am. Chem. Soc.*, **68**, 2204 (1946).
6. R. Streck, *J. Organomet. Chem.*, **71**, 181 (1974).
7. R. Tarao, S. Takeda, *Bull. Chem. Soc. Jpn.*, **40**, 650 (1967).
8. A. Zambelli, J. DiPietro, G. Gatti, *J. Poly. Sci., A1*, 403 (1963).
9. K. Ziegler, R. Köster, H. Lehmkuhl, R. Reinert, *Justus Liebigs Ann. Chem.*, **629**, 33 (1960).
10. H. Martin, R. Reinacker, K. Ziegler, *Brennst. Chem.*, **47**, 33 (1966); see p. 72, ref. 1.
11. K. Ziegler, R. Köster, *Justus Liebigs Ann. Chem.*, **608**, 1, 4 (1957).
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5.3.3.3.3. by the Interaction with an Active-Metal Hydride and Olefin.

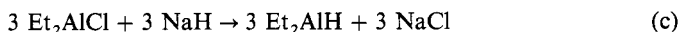
Before the direct synthesis of trialkylaluminums:



was known¹⁻³, other comparatively cheap starting materials were $AlCl_3$, NaH and an olefin. The principles are the same as for hydroalumination of olefins (see §5.3.3.4.1), for the start of the reaction cycle is redistribution (see §5.3.3.3.2) of R_3Al (shown for $R = Et$) with $AlCl_3$:



followed by reaction of R_2AlCl with NaH to give R_2AlH :



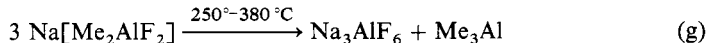
5.3. Formation of Bonds

5.3.3. Formation of Carbon—Al Bonds

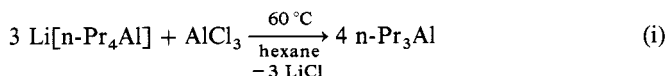
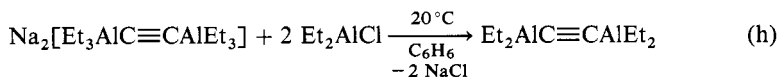
5.3.3.3. from Al Halides or Organoaluminum Halides

convenient to obtain¹¹ R_2AlF from the reaction between R_2AlCl and finely powdered NaF.

Dimethylaluminum fluoride is an intermediate in the preparation of Me_3Al via Me_2AlCl in the presence of NaF. The equilibrium in Eq. (g) is shifted to the right owing to the formation¹¹ of the stable Na_3AlF_6 :



Finally, tetraorganoaluminates react with Al halides to give organoaluminum compounds^{1,2,12}:

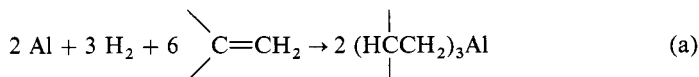


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1. H. Lehmkuhl, K. Ziegler, *Aluminium-Organische Verbindungen*, in *Methoden der Organischen Chemie* (Houben Weyl), E. Müller, ed., Vol. 13/4, Georg Thieme Verlag, Stuttgart, 1970, p. 58.
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5.3.3.3.3. by the Interaction with an Active-Metal Hydride and Olefin.

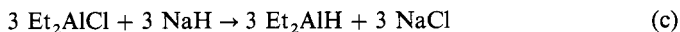
Before the direct synthesis of trialkylaluminums:



was known¹⁻³, other comparatively cheap starting materials were $AlCl_3$, NaH and an olefin. The principles are the same as for hydroalumination of olefins (see §5.3.3.4.1), for the start of the reaction cycle is redistribution (see §5.3.3.2) of R_3Al (shown for $R = Et$) with $AlCl_3$:



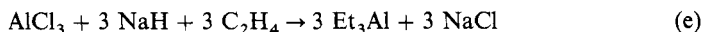
followed by reaction of R_2AlCl with NaH to give R_2AlH :



which hydroaluminates the olefin. Therefore, starting with 2 mol of R_3Al [Eq. (b)], 3 mol R_3Al are obtained:



The overall reaction is¹:



These reactions depend critically on reagents and conditions in order to obtain the theoretical growth factor¹ of 1.5.

Using the available ethylaluminum sesquichloride (see §5.3.3.2.2) instead of $AlCl_3$, a growth factor of three can be obtained¹.

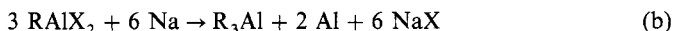
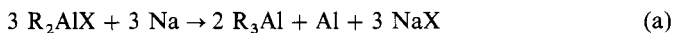
(B. WRACKMEYER)

1. H. Lehmkuhl, K. Ziegler, *Aluminium-Organische Verbindungen*, in *Methoden der Organischen Chemie (Houben Weyl)*, E. Müller, ed., Vol. 13/4, Georg Thieme Verlag, Stuttgart, 1970, p.58.

5.3.3.3.4. by the Dehalogenation of R_nAlX_{3-n} with Active Metals.

The dehalogenation of organoaluminum halides with active metals, such as Na, K is still of importance considering the easy access to the organoaluminum sesquihalides (see §5.3.3.2.2)^{1,2,5}.

The reaction proceeds via the formation of R_3Al , metallic Al and NaX :

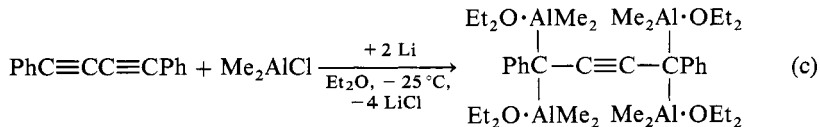


For $X = Cl$ and $R =$ alkyl, no solvent is required, although the reaction should be conducted in at least two steps with intermediate distillation of a crude product¹. Using $X = Br, I$ and $R =$ alkyl xylene or decane facilitates the reaction^{1,2}. For $X = Cl, R = Ph$ xylene is used and a 59 % yield of Ph_3Al results¹ starting from $Ph_3Al_2Cl_3$.

The stoichiometry is important, since xs Na leads to formation of $NaAlR_4$.

Modifications are possible^{1,2}. Thus ethylaluminum sesquichloride can be converted quantitatively to Et_2AlCl . Another advantage is the precipitation of finely divided and active Al metal³. This can again be utilized in the preparation of aluminum sesquihalides.

In the presence of ether and unsaturated compounds, the reaction between R_2AlCl and alkali metal may give not R_3Al but addition products⁴, instead, e.g., triorgano aluminums⁵:



(B. WRACKMEYER)

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5.3. Formation of Bonds

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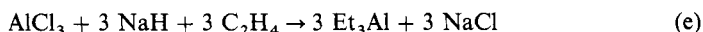
5.3.3. Formation of Carbon—Al Bonds

5.3.3.3. from Al Halides or Organoaluminum Halides

which hydroaluminates the olefin. Therefore, starting with 2 mol of R_3Al [Eq. (b)], 3 mol R_3Al are obtained:



The overall reaction is¹:



These reactions depend critically on reagents and conditions in order to obtain the theoretical growth factor¹ of 1.5.

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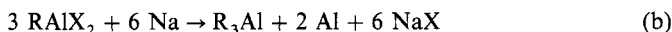
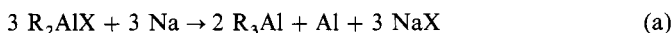
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5.3.3.3.4. by the Dehalogenation of R_nAlX_{3-n} with Active Metals.

The dehalogenation of organoaluminum halides with active metals, such as Na, K is still of importance considering the easy access to the organoaluminum sesquihalides (see §5.3.3.2.2)^{1,2,5}.

The reaction proceeds via the formation of R_3Al , metallic Al and NaX :

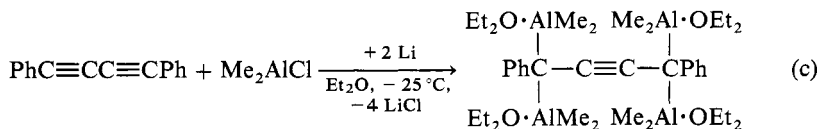


For $X = Cl$ and $R =$ alkyl, no solvent is required, although the reaction should be conducted in at least two steps with intermediate distillation of a crude product¹. Using $X = Br, I$ and $R =$ alkyl xylene or decane facilitates the reaction^{1,2}. For $X = Cl, R = Ph$ xylene is used and a 59% yield of Ph_3Al results¹ starting from $Ph_3Al_2Cl_3$.

The stoichiometry is important, since xs Na leads to formation of $NaAlR_4$.

Modifications are possible^{1,2}. Thus ethylaluminum sesquichloride can be converted quantitatively to Et_2AlCl . Another advantage is the precipitation of finely divided and active Al metal³. This can again be utilized in the preparation of aluminum sesquihalides.

In the presence of ether and unsaturated compounds, the reaction between R_2AlCl and alkali metal may give not R_3Al but addition products⁴, instead, e.g., triorgano aluminums⁵:



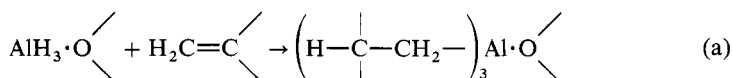
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5.3.3.4. from Al Hydrides or Complex Al Hydrides**5.3.3.4.1. by Addition to Olefins or Acetylenes (Hydroalumination).**

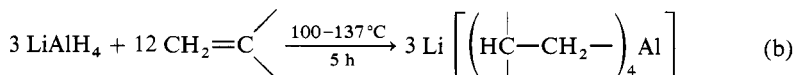
The Al—H bond offers synthetic possibilities in organic and organometallic chemistry¹⁻⁴. Various Al—H compounds [e.g., (AlH₃)_x(OEt₂)_y, R₂AlH, R₂AlH complexes, LiAlH₄ or NaAlH₄ in various solvents, with or without catalysts] show different behaviors toward olefins and acetylenes. The proper choice of a suitable Al—H compound as well as of the conditions is essential for the successful formation of Al—C bonds. The main sources for Al—H bonds are Li[AlH₄]⁵ and R₂AlH (R = Et, i-Bu, best obtained in the first step of the direct synthesis⁶ (see §5.3.3.2.1).

Aluminum hydride, AlH₃, can be prepared from the tetrahydroaluminates with acids (e.g., AlCl₃, H₂SO₄) in ethers. It is used in solution or as a solid that still contains ether. Aluminum hydride adds to olefins (e.g., C₂H₄, C₃H₆, i-C₄H₈) to give the trialkylaluminum ether complexes or mixtures of R₃Al and ether adducts¹:

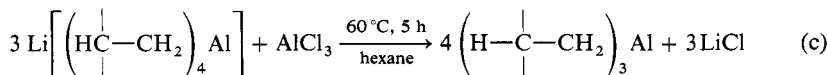


Because it is difficult to remove the ether, this method is not popular.

The tetrahydroaluminates are more available and easier to handle than AlH₃. Ether-free trialkylaluminums can be prepared^{1,9} (> 80% yield) starting from LiAlH₄:

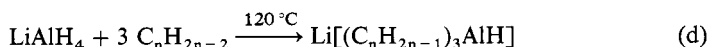


The tetraalkylaluminate is obtained quantitatively and reacts readily with a suspension of AlCl₃ in hexane (prepared in a ball mill):



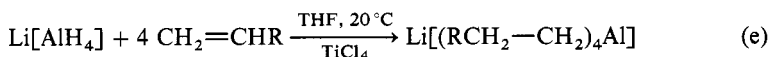
With branched olefins (e.g., isobutene), reaction (b) stops at the [R₃AlH][−] anion. Sodium tetrahydroaluminate requires catalytic amounts of LiAlH₄, R₃Al or certain metal halides to react with ethylene or terminal olefins¹⁰.

Acyclic, nonterminal olefins do not react with LiAlH₄ according to Eq. (b). However, addition of LiAlH₄ to cyclopentene, cycloheptene and cyclooctene occurs slowly at 120°C to give the tricycloalkylhydroaluminates⁹:

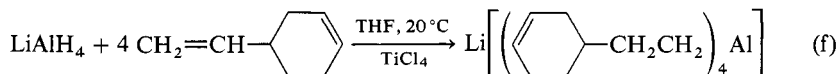


Cyclohexene shows a low reactivity toward LiAlH₄, indicating that ring size and strain at the C=C double bond is important in the course of reaction (d).

The conditions required for the reactions (a), (b) and (d) (autoclave, high H₂ and olefin P) are not suitable for laboratory work. However, alkylaluminates can be prepared by the hydroalumination of multiple C—C bonds with LiAlH₄ in the presence of transition-metal salts in tetrahydrofuran (THF)¹¹⁻¹⁴:

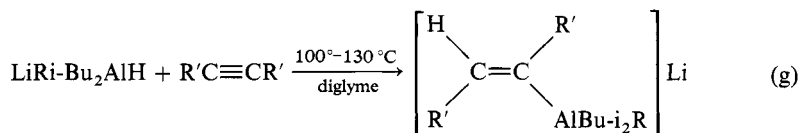


where TiCl_4 ¹¹⁻¹³, (TiCl_3) , $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ ¹⁴ are active catalysts. As for other transition-metal halides only for $\text{M} = \text{Zr}, \text{Co}, \text{Ni}$ is catalytic activity found¹³. In the hydroalumination of alkenes with the $\text{LiAlH}_4\text{-TiCl}_4$ system for a particular alkene, hex-1-ene, the reactivity decreases in the series¹¹: $\text{LiAlH}_4 > \text{AlH}_3 > \text{AlH}_2\text{Cl} > \text{AlHCl}_2$. The reactivity of the alkenes toward $\text{LiAlH}_4\text{-TiCl}_4$ decreases in the series¹¹: $\text{CH}_2=\text{CHR} > \text{CH}_2=\text{CR}_2 > \text{RCH}=\text{CHR}$. Thus dienes can be hydroaluminated selectively at the terminal double bond^{11,15}, e.g.:



Hydroalumination of nonterminal olefins may be accompanied by isomerization to the terminal olefins, depending on the $\text{Al-H}:\text{Ti}$ ratio¹¹. The tetraalkylaluminates accessible via reaction (e) or (f) are useful in organic synthesis¹¹⁻¹⁶.

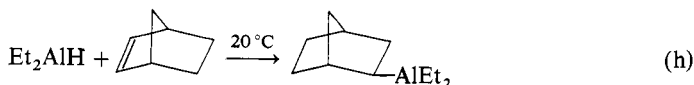
Terminal alkynes with tetrahydroaluminates lead to substitution of the acidic hydrogen (see §5.3.3.5.2). However, in the presence of a small amount of $i\text{-Bu}_2\text{AlH}$ more than 90% hydroalumination product is obtained when NaAlH_4 and phenyl ethyne react in diglyme¹⁷. This is a useful method of trans-hydroalumination of acetylenes, mainly 1,2-dialkylacetylenes, by using LiAlH_4 ^{18,19} or Li diisobutyl alkylaluminates^{20,21} in ethers e.g.:



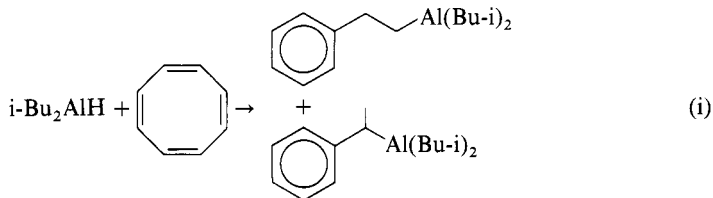
The aluminates are not isolated. The structures are deduced from the products obtained by hydrolysis or other reactions.

The second step of the direct synthesis^{1,6} (see §5.3.3.2.1) involves the hydroalumination of olefins by R_2AlH . This makes possible synthesis of unsymmetrical trialkylaluminums, $\text{R}_2\text{AlR}'$. However, the $\text{R}_2\text{AlR}'$ compounds undergo spontaneous redistribution of the groups R and R' , leading to mixtures of trialkylaluminums consisting of R_3Al , $\text{R}_2\text{AlR}'$, RAIR''_2 and AlR_3 . Attempts to purify this mixture may lead to complete transalkylation if a volatile olefin can be eliminated and removed from the reaction mixture (see §5.3.3.4.2).

The rates of hydroalumination of various alkenes by Et_2AlH indicates that dissociation of the trimeric Et_2AlH is a first step. The reactivity order is²²: $\text{CH}_2=\text{CHR} > \text{CH}_2=\text{CRR}' > \text{RCH}=\text{CHR}'$. Similar results emerge from the hydroalumination of isomeric undecenes²³. In the presence of 3 mol% of $\text{Ti}(\text{OBu-}n)_4$, the rate of addition of $i\text{-Bu}_2\text{AlH}$ to trans-undec-5-ene is increased 100-fold. The hydroalumination of cis-cycloolefins depends on ring size, as is evident from the short half-lives of C_4H_6 , C_5H_8 , C_7H_{12} , C_8H_{14} and C_9H_{16} and the longer half-lives of C_6H_{10} , $\text{C}_{10}\text{H}_{18}$ and $\text{C}_{11}\text{H}_{20}$ ²². Strain at the $\text{C}=\text{C}$ double bond shortens the half-life of trans-cyclononene in the presence of Et_2AlH by a factor ≥ 280 as compared to cis-cyclononene²⁴. The strained double bond in bicyclo[2.2.1]hept-2-ene accounts for its smooth reaction with Et_2AlH ²⁵:



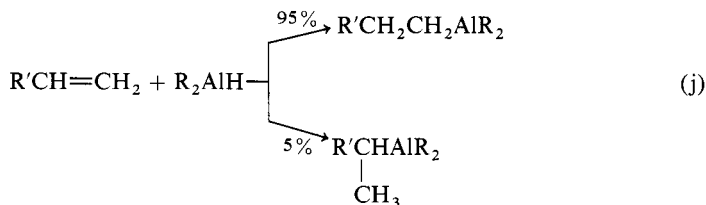
Cyclooctatetraene reacts with $i\text{-Bu}_2\text{AlH}$ to give two different benzene derivatives:



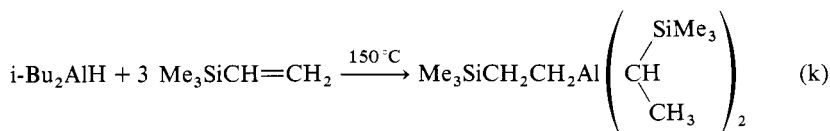
The intermediacy of bicyclo[4.2.0]octa-2,4,7-triene accounts for these products²⁶.

The addition of Al—H bonds to alkenes is accelerated by catalytic amounts of transition-metal compounds^{1,23}, whereas donor solvents slow the hydroalumination.

The hydroalumination of alk-1-enes is regioselective, placing Al at the terminal carbon (95%):

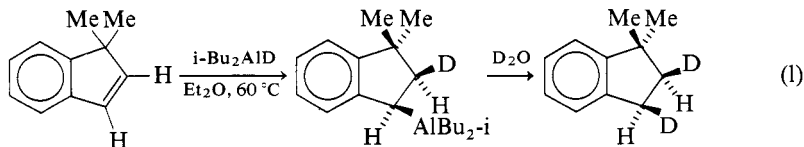


Exceptions are styrene²⁷ (25% nonterminal) and $\text{Et}_3\text{SiCH}=\text{CH}_2$ (70% nonterminal)²⁸. The hydroalumination of $\text{Me}_3\text{SiCH}=\text{CH}_2$ with $i\text{-Bu}_2\text{AlH}$ followed by olefin displacement (see §5.3.3.4.2) leads to a single product²⁹:



The first two steps are regioselective with the Al at the nonterminal position and the final step is controlled by steric interactions²⁹.

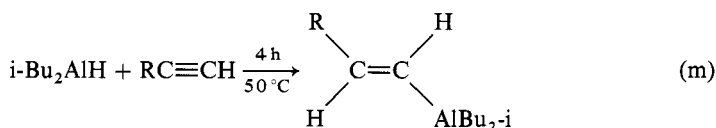
The cis-stereochemistry of the hydroalumination of olefins is proved by the reaction of a strained cycloolefin, 1,1-dimethylindene, with $i\text{-Bu}_2\text{AlD}$ in the presence of Et_2O (to slow down the inversion process of the Al—C bond). The deuterolysis of the Al—C bond (retention of configuration) leads to pure cis-2,3-dideuterio-1,1-dimethylindane³⁰:



In the hydroalumination of cyclic olefins with $i\text{-Bu}_2\text{AlH}$ the cis-addition in donor solvents is kinetically controlled⁵⁰. For indenenes, polar effects are noticeable, whereas steric effects are most important for 1-substituted acenaphthenes⁵⁰. The regiochemistry of the addition is controlled by steric effects except for trimethylsilyl substituents⁵⁰. The

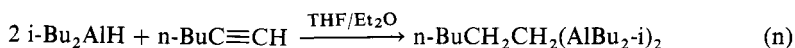
reactivity of the cyclic olefins towards $i\text{-Bu}_2\text{AlH}$ decreases: acenaphthylene, 1,1-dimethyl-3-trimethylsilylindene, 1-methylacenaphthylene, 1,1-dimethylindene, 1-phenylacenaphthylene, 1,1-dimethyl-3-phenylindene.

The reaction of dialkylaluminum hydrides with mono- or di-substituted acetylenes provides the best route to alkenyldialkylaluminums^{31,32}. The hydroalumination of acetylene itself gives polymers¹. Monohydroalumination of terminal acetylenes can be conducted either neat or in hydrocarbon solvents ($\leq 50^\circ\text{C}$). The products are (E)-alkenylalanes as the result of a regio and stereoselective cis addition of Al—H to the $\text{C}\equiv\text{C}$ bond^{31,32}:

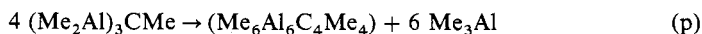
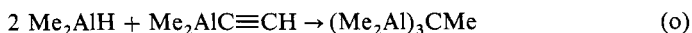


Deuterolysis gives the trans-deuterio-olefin, and small amounts of 1-deuterio-hex-1-yne (metallation) and 1,1-dideuterio-n-hexane (bis-hydroalumination). The predictable stereochemistry, the available starting materials and the known reactivity pattern of Al—C= bonds encourages synthetic application of this reaction^{3,4,33–36}. The R group at the $\text{C}\equiv\text{C}$ bond influences reaction (m): secondary or tertiary alkyl groups increase the rate; more acidic alk-1-ynes (e.g. $\text{R} = \text{Ph}$, olefin) increases the amount of metallation³.

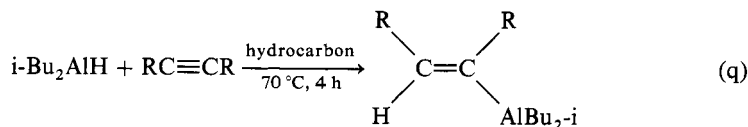
Solvent is important in the hydroalumination of terminal $\text{C}\equiv\text{C}$ bonds³⁷. Reaction of hex-1-yne alkyne with 2 mol $i\text{-Bu}_2\text{AlH}$ neat or in THF gives the bis-hydroalumination product^{31,38,39}:



Metallation occurs⁴⁰ in tertiary amines (see §5.3.3.5.2), and the 1,1,1-tris-alumino alkanes are obtained via bis-hydroalumination of the dialkylalkynylaluminum initially formed⁴¹. This is used to prepare decamethylhexaaluminaadamantane⁴²:



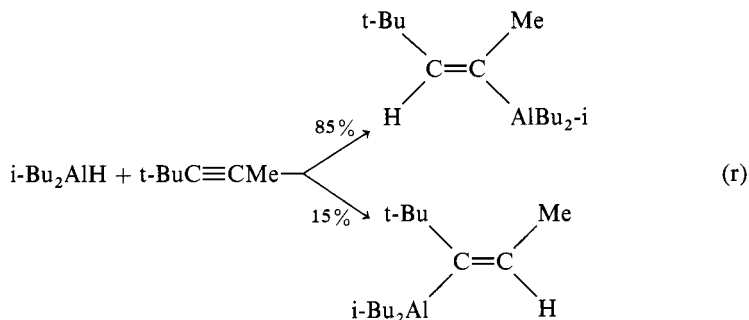
In contrast to the low reactivity of internal olefins toward R_2AlH , carbon-1,2-disubstituted acetylenes react ($50\text{--}70^\circ\text{C}$, in hydrocarbons, within a few hours) to give high yields of (E)-alkenylaluminums^{31,32}:



Isomerization to the (Z) isomers may occur after prolonged heating (e.g., for $\text{R} = \text{aryl}$), and small amounts of dienyraluminums (addition of alkenylaluminums to the unreacted alkyne; see §5.3.3.5.1) are observed.

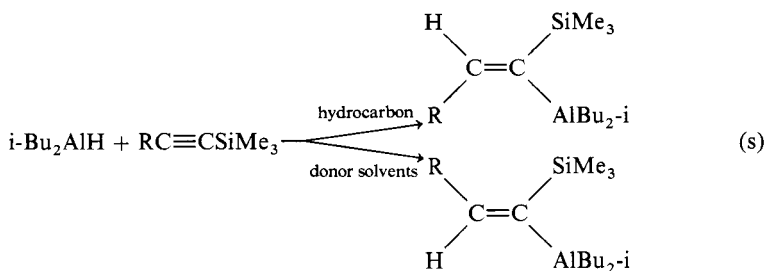
The rate of hydroalumination of the internal acetylenes decreases in the series³⁰: $t\text{-BuC}\equiv\text{CBu-t} > n\text{-BuC}\equiv\text{CBu-n} > \text{PhC}\equiv\text{CPh}$.

In donor solvents (Et_2O , THF, R_3N) the rate of hydroalumination is slower than with hydrocarbons. Nickel compounds catalyze the reaction, but isomerization may take place more readily⁴³. The regiospecificity of cis-hydroalumination of 1,2-disubstituted acetylenes with $i\text{-Bu}_2\text{AlH}$ is inferior to dialkylboranes (see §5.3.2.5.1)³:



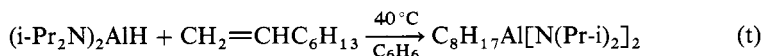
Hydroboration analogous to Eq. (r) with $(\text{cyclo-C}_6\text{H}_{11})_2\text{BH}$ yields⁴⁴ the alkenes in ratio of 97:3 instead of 85:15 for hydroalumination.

The stereo- and regiospecificity of the addition of Al—H bonds to heteroatom-substituted acetylenes is determined by the conditions. The reaction of (1-alkynyl)trimethylsilanes with $i\text{-Bu}_2\text{AlH}$ in ether gives the (E) isomer with Al and Si attached to the same carbon atom⁴⁵, whereas in hydrocarbon solvent the E isomer, initially formed, isomerizes rapidly to give the (Z) isomer⁴⁶:



The hydroalumination of alkynes by $i\text{-Bu}_2\text{AlH}$ proceeds readily⁴⁹ in the presence of $\text{BrCu}\cdot 2\text{LiCl}$ or $\text{CH}_3\text{Cu}\cdot\text{MgClAr}\cdot 2\text{LiCl}$ in THF at -20°C .

Finally, bis(dialkylamino)aluminum hydrides react with unsaturated carbon-carbon bonds. In the presence of catalytic amounts of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ the reaction is complete within 10 min (93% yield)^{47,48}:



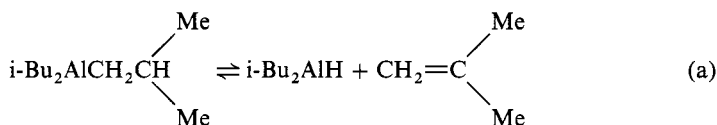
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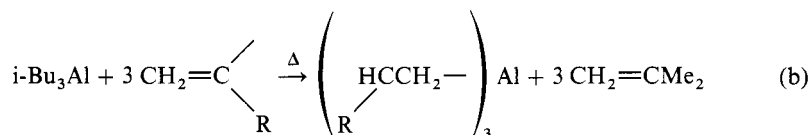
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5.3.3.4.2. by Transfer of Al Hydride from One Olefin to Another—Al Alkyl—Olefin Displacement.

Trialkylaluminums eliminate olefin leading to a dialkylaluminum hydride as shown for the most important example, $i\text{-Bu}_3\text{Al}$:

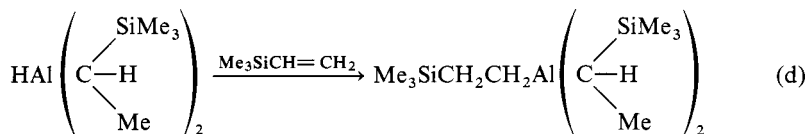
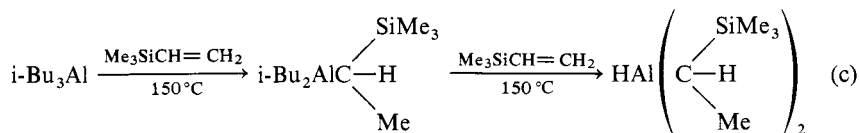


Equilibrium (a) is shifted to the right at $>100^\circ\text{C}$. The addition of a second terminal olefin, $\text{CH}_2=\text{CHR}$ or $\text{CH}_2=\text{CRR}'$, opens a way to $i\text{-Bu}_2\text{AlCH}_2\text{CH}_2\text{R}$ or $i\text{-Bu}_2\text{AlCH}_2\text{CHRR}'$. These compounds may again lose isobutene followed by hydroalumination of the other olefin present. Continual removal of the isobutene finally leads to new R_3Al :



This olefin displacement is the result of elimination and addition¹⁻⁴. This displacement presents no problem when true homologues of isobutene are used (e.g., 2-ethylhex-1-ene³, 2-phenylpropene⁵).

With terminal olefins, $\text{CH}_2=\text{CHR}$, the addition of the $\text{Al}-\text{C}$ bond across the double bond also needs to be considered (growth reaction, see §5.3.3.5.1). Because $>100^\circ\text{C}$ is required to achieve the displacement, conditions must be controlled to avoid isomerization of the olefin¹: (1) the addition of the n -alkene to $i\text{-Bu}_3\text{Al}$ at 120°C is performed at a rate so that $x\text{s } \text{R}_2\text{AlH}$ is present to prevent side reactions; (2) elimination and addition are conducted in several steps at higher and lower T , respectively. The latter procedure works because the tendency for olefin elimination decreases: $\text{AlCH}_2\text{CH} \lt \text{AlCH}_2\text{CH}_2- > \text{AlCH}_2\text{CH}_3$. Displacement with terminal olefins leads to formation of primary $\text{Al}-\text{C}$ bonds. Exceptions are styrene⁶ (ca. 25% secondary $\text{Al}-\text{C}$ bonds), which gives a mixture of compounds, in contrast to $\text{PhCMe}=\text{CH}_2$ (α -methylstyrene), which gives exclusively⁵ $(\text{PhHCMe}-\text{CH}_2)_3\text{Al}$. The 1:3 reaction between $i\text{-Bu}_3\text{Al}$ and of $\text{Me}_3\text{SiCH}=\text{CH}_2$ leads to a single compound, and the structure indicates that secondary $\text{Al}-\text{C}$ bonds are formed in the first two steps⁷:



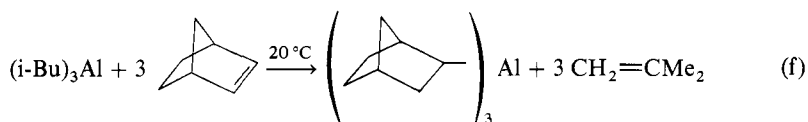
The rate of olefin elimination is enhanced by catalytic amounts of Ni compounds, which suppress the growth reaction (in contrast to compounds of Ti, Zr or V); however, they also catalyze double-bond migration and often the catalytic activity rapidly decreases¹. The catalysis of the displacement reaction is of interest for the preparation of Et₃Al or Pr₃Al from i-Bu₃Al, because no isomerization of the olefin can occur and the conditions (50–100°C, Ni) exclude the growth reaction¹.

Cycloolefins and nonterminal olefins, although less reactive than terminal olefins, also enter into displacement⁸. Starting from i-Bu₃Al and keeping T = 135°C with continual removal of isobutene di-s-alkylaluminum hydrides are obtained in good yield⁸:

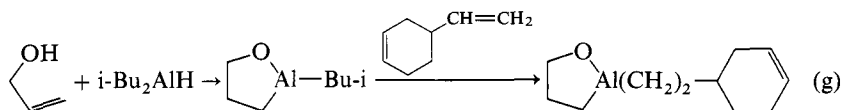


At > 150°C isomerization occurs depending on the structure of the olefin⁸.

Whereas displacement with cyclohexene requires the use of an autoclave, the C=C bonds in strained ring systems are more reactive, e.g., in bicyclo[2.2.1]hept-2-ene with i-Bu₃Al at 20°C. It gives ca. 50% of the displacement product and 50% addition of i-Bu₃Al across the reactive double bond⁹ (see §5.3.3.5.1):



The hydroalumination of functionally substituted alkenes can be combined with displacement¹⁰:



The combination of the direct synthesis¹ of i-Bu₂AlH or i-Bu₃Al (see §5.3.3.2.1) with the olefin displacement reaction opens a useful route to new organoaluminums.

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5.3.3.4.3. by Redistribution with Organoaluminums.

Organoaluminum hydrides can be prepared by redistribution^{1–4}. Aluminum hydride, available from the reaction of tetrahydroaluminates with AlCl₃ in ethers^{1,2}, is a

5.3. Formation of Bonds

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5.3.3. Formation of Carbon—Al Bonds

5.3.3.4. from Al Hydrides or Complex Al Hydrides

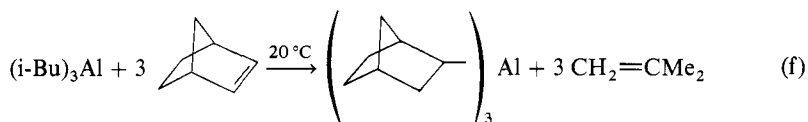
The rate of olefin elimination is enhanced by catalytic amounts of Ni compounds, which suppress the growth reaction (in contrast to compounds of Ti, Zr or V); however, they also catalyze double-bond migration and often the catalytic activity rapidly decreases¹. The catalysis of the displacement reaction is of interest for the preparation of Et₃Al or Pr₃Al from i-Bu₃Al, because no isomerization of the olefin can occur and the conditions (50–100°C, Ni) exclude the growth reaction¹.

Cycloolefins and nonterminal olefins, although less reactive than terminal olefins, also enter into displacement⁸. Starting from i-Bu₃Al and keeping T = 135°C with continual removal of isobutene di-s-alkylaluminum hydrides are obtained in good yield⁸:

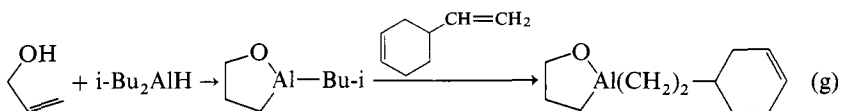


At > 150°C isomerization occurs depending on the structure of the olefin⁸.

Whereas displacement with cyclohexene requires the use of an autoclave, the C=C bonds in strained ring systems are more reactive, e.g., in bicyclo[2.2.1]hept-2-ene with i-Bu₃Al at 20°C. It gives ca. 50% of the displacement product and 50% addition of i-Bu₃Al across the reactive double bond⁹ (see §5.3.3.5.1):



The hydroalumination of functionally substituted alkenes can be combined with displacement¹⁰:



The combination of the direct synthesis¹ of i-Bu₂AlH or i-Bu₃Al (see §5.3.3.2.1) with the olefin displacement reaction opens a useful route to new organoaluminums.

(B. WRACKMEYER)

1. H. Lehmkuhl, K. Ziegler, *Aluminium-Organische Verbindungen*, in *Methoden der Organischen Chemie* (Houben-Weyl), E. Müller, ed., Vol. 13/4, Georg Thieme Verlag, Stuttgart, 1970, p. 39.
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3. K. Ziegler, H. Martin, F. Krupp, *Justus Liebigs Ann. Chem.*, 629, 14 (1960).
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6. G. Natta, P. Pino, G. Mazzanti, P. Longi, P. Bernardini, *J. Am. Chem. Soc.*, 81, 2561 (1959).
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10. K. Isagawa, K. Tatsumi, Y. Otsuji, *Chem. Lett.*, 1145 (1976).

5.3.3.4.3. by Redistribution with Organoaluminums.

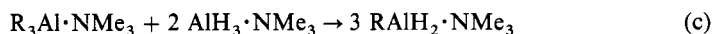
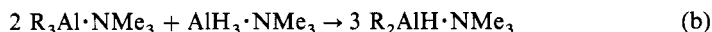
Organoaluminum hydrides can be prepared by redistribution^{1–4}. Aluminum hydride, available from the reaction of tetrahydroaluminates with AlCl₃ in ethers^{1,2}, is a

suitable starting material. Reaction of $\text{AlH}_3 \cdot \text{OEt}_2$ with triorganoaluminums leads to organoaluminum hydrides⁵, e.g., Ph_2AlH :

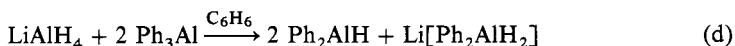


Many R_2AlH compounds are trimeric^{1,2} with strong hydride bridges, because they can be obtained ether-free from ethereal solutions.

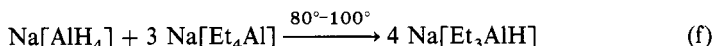
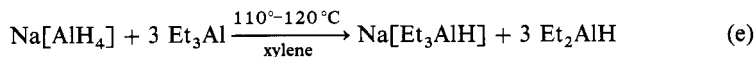
The trimethylamine complex $\text{H}_3\text{Al} \cdot \text{NMe}_3$ is another reagent in redistribution. It reacts with the $\text{R}_3\text{Al} \cdot \text{NMe}_3$ ($\text{R} = \text{Me}, \text{Et}$) complexes stoichiometrically to give^{6,7} the Me_3N complexes of R_2AlH and RAIH_2 . The RAIH_2 compounds are unstable in ethers or in nondonor solvents:



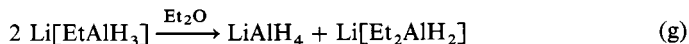
The tetrahydroaluminates themselves can undergo redistribution reactions with organoaluminums. Thus, Ph_2AlH can also be prepared⁵ from Ph_3Al and LiAlH_4 :



A good yield of triethylhydroaluminate is obtained either from⁸ $\text{Na}[\text{AlH}_4]$ and Et_3Al or from⁹ $\text{Na}[\text{Et}_4\text{Al}]$:



Reactions similar to Eqs. (e) and (f) lead to the diethyldihydroaluminates⁴. The alkyltrihydroaluminates, $[\text{RAIH}_3]^-$, are not well characterized. In the absence of solvent, Et_3Al reacts with LiAlH_4 at 100°C to give $\text{Li}[\text{EtAlH}_3]$, but the corresponding sodium salt is not available by this method⁹. The reaction of LiAlH_4 with $\text{Li}[\text{Et}_4\text{Al}]$ (3:1) in ether is an equilibrium that lies¹⁰ at the side of LiAlH_4 and $\text{Li}[\text{Et}_2\text{AlH}_2]$:



Isobutyltrihydroaluminate $\text{Na}[\text{i-BuAlH}_3]$ can be prepared¹¹ in tetrahydrofuran (THF) from $\text{Na}[\text{AlH}_4]$ and $\text{i-Bu}_3\text{Al}$. Ether cleavage leads to the formation of $\text{i-Bu}_2\text{AlOBU-n}$:



The analogous reaction with Et_3Al in THF also gives the ether cleavage product, but the $\text{Na}[\text{Et}_2\text{AlH}_2]$ is obtained¹¹.

(B. WRACKMEYER)

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2. E. Wiberg, E. Amberger, *Hydrides*, Elsevier, Amsterdam, 1971, p. 381.
3. T. Mole, *Organomet. React.* **1**, 1 (1970).
4. T. Mole, E. A. Jeffery, *Organoaluminum Compounds*, Elsevier, Amsterdam, 1972, p. 53.
5. J. R. Surtees, *Chem. Ind. (London)*, 1260 (1964).
6. F. M. Peters, B. Bartocha, A. J. Bilbo, *Can. J. Chem.*, **41**, 1051 (1963).
7. F. M. Peters, B. Bartocha, *Chem. Ind. (London)*, 1271 (1961).

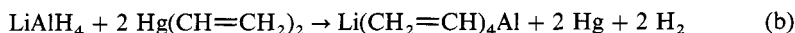
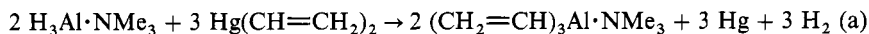
8. L. I. Zakharkin, V. V. Gavrilenko, V. K. Golubev, *Bull. Acad. Sci. USSR, (Engl. Transl.)*, 117 (1966).
9. P. Kobetz, W. E. Becker, R. C. Pinkerton, J. B. Honeycutt, *Inorg. Chem.*, 2, 859 (1963).
10. E. C. Ashby, R. G. Bech, *Inorg. Chem.*, 9, 2300 (1970).
11. L. I. Zakharkin, V. V. Gavrilenko, *Bull. Akad. Sci. USSR (Engl. Transl.)*, 624 (1965).

5.3.3.4.4. by Exchange with Other Organometallics.

Organoaluminum hydrides or complex aluminum hydrides can accept organic groups from other organoelement compounds. Either the hydride or another organic group is exchanged¹. There is practical interest in these exchanges when the element hydride decomposes into H₂ and the element (e.g., Hg), or when the element hydride is insoluble and separates readily (e.g., MgH₂, ZnH₂)².

Many organomercurials form C—Al bonds via hydride—organyl exchange. Diethylmercury reacts with Et₂AlH to give Et₃Al, elemental Hg, H₂ and ethane (with Et₂Cd or Et₂Zn, deposition of Zn or Cd and H₂ is observed, whereas with Et₂Mg, MgH₂ is formed)³.

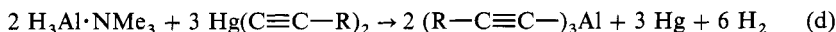
The reactivity of aluminum hydrides toward organomercurials decreases⁴: LiAlH₄ > H₃Al·NMe₃. The reaction of Al hydrides with alkenylmercurials gives alkenyl aluminums⁴⁻⁷:



This includes the preparation of (CF₂=CF)₃Al⁷ and trimethylamine complexes of vinylaluminum hydrides. The phenyl group is exchanged between an aminoalane and diphenylmercury⁴:

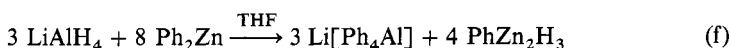
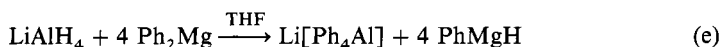


The Me₃N complexes of trialkynylaluminums are obtained^{4,8} from bis(alkynyl)mercury with H₃Al·NMe₃:



Similarly, the tetraalkynylaluminates, Li[(R—C≡C)₄Al], are accessible from the reaction of LiAlH₄ with (RC≡C)₂Hg although ca. 5-10% of the alkynyl groups are further reduced⁸.

Metal alkyls (MeLi, Me₂Be, Et₂Mg, Me₂Zn, Me₂Cd) react with LiAlH₄ to give the corresponding metal hydrides and the alkylhydridoaluminates⁹. Methylberyllium hydride can be obtained from xs Me₂Be and Me₂AlH in ether⁹. With some metal aryls (Ph₂Mg¹⁰, Ph₂Zn¹¹) and LiAlH₄, the conditions determine the nature of the products. In Et₂O the reaction leads to the metal hydrides, whereas in tetrahydrofuran (THF) arylmetalhydrides are obtained in addition to the tetraphenylaluminates:



5.3. Formation of Bonds

149

5.3.3. Formation of Carbon—Al Bonds

5.3.3.4. from Al Hydrides or Complex Al Hydrides

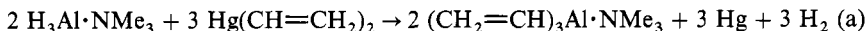
8. L. I. Zakharkin, V. V. Gavrilenko, V. K. Golubev, *Bull. Acad. Sci. USSR, (Engl. Transl.)*, 117 (1966).
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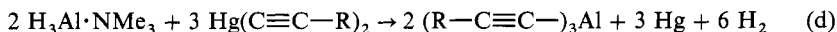
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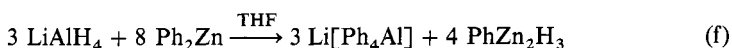
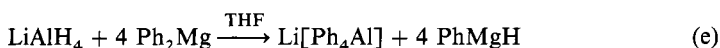


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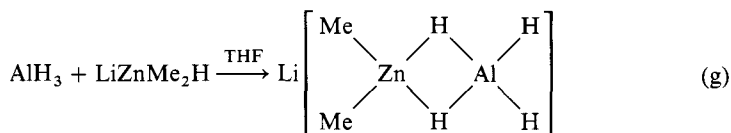


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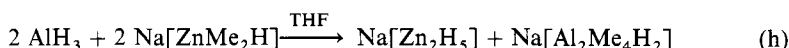
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If LiAlH_4 is added to Me_2Zn in THF, soluble triple-metal complexes are obtained instead of insoluble ZnH_2 and various methylhydridoaluminates^{12,13}. The same result is observed when $\text{H}_3\text{Al}\cdot\text{THF}$ in THF reacts with LiZnMe_2H :



However, if the reaction is carried out with $\text{Na}[\text{ZnMe}_2\text{H}]$ or $\text{K}[\text{ZnMe}_2\text{H}]$, complex Zn hydrides are formed with Na (K) Al triple complexes¹²:



(B. WRACKMEYER)

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3. L. I. Zakharkin, I. M. Khorlina, *J. Gen. Chem. USSR (Engl. Transl.)*, **32**, 2740 (1962).
4. J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961).
5. B. Bartocha, A. J. Bilbo, D. E. Bublit, M. Y. Gray, *Angew. Chem.*, **72**, 36 (1960).
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7. B. Bartocha, A. J. Bilbo, *J. Am. Chem. Soc.*, **83**, 2202 (1961).
8. P. Chini, A. Baradel, E. Pauluzzi, M. DeMalde, *Chim. Ind.*, **44**, 1220 (1962).
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13. J. J. Watkins, E. C. Ashby, *Inorg. Chem.*, **16**, 2070 (1977).

5.3.3.5. from Other Organoaluminum Compounds

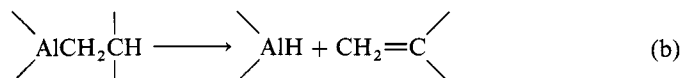
5.3.3.5.1. by Addition of R—Al Bonds to Olefins or Acetylenes (Carbalumination).

The addition of the C—Al bond to olefinic or acetylenic substrates (carbalumination) is of interest in organometallic synthesis¹⁻⁸.

Trialkylaluminums and olefins can enter into olefin displacements (see §5.3.3.4.2) or addition of the C—Al bond to the C=C bond occurs:



If olefin elimination can be avoided, the repeated addition of the new trialkylaluminum to the olefin opens a route to long-chain alkyl groups:



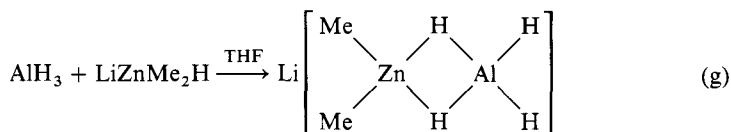
This is called the growth reaction^{1,4}.

5.3. Formation of Bonds

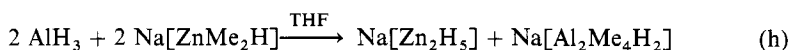
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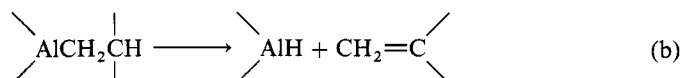
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The addition of the C—Al bond to olefinic or acetylenic substrates (carbalumination) is of interest in organometallic synthesis¹⁻⁸.

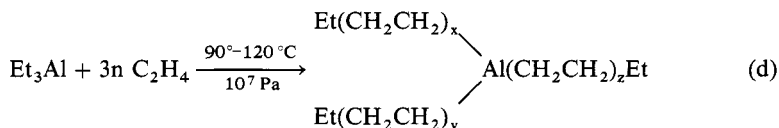
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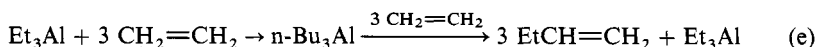
If olefin elimination can be avoided, the repeated addition of the new trialkylaluminum to the olefin opens a route to long-chain alkyl groups:



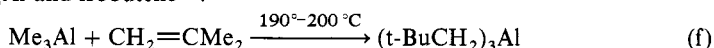
This is called the growth reaction^{1,4}.

$$\text{Al} + \frac{3}{2}\text{H}_2 + 3\text{C}_2\text{H}_4 \xrightarrow[10^7 \text{ Pa}]{90^\circ-120^\circ \text{C}} \text{Et}_3\text{Al} \quad (\text{c})$$


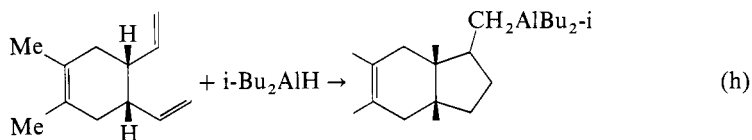
The carbalumination of olefins followed by displacement is valuable in organic synthesis (e.g., in the dimerization of olefins, synthesis of long-chain, terminal olefins)^{4,5}:



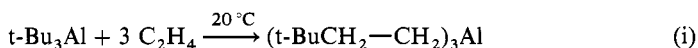
Primary, odd-numbered aliphatic compounds are prepared from ethylene and $n\text{-Pr}_3\text{Al}$ (Me_3Al is not suitable owing to strong association under the reaction conditions⁴) employing conditions similar to those⁴ for Et_3Al . The reaction of 1,1-dialkylethylenes with R_3Al is complicated by olefin displacement equilibria. However, with Me_3Al this problem does not arise. To increase the amount of monomeric Me_3Al that enters carbalumination T is kept at 190–200°C. This leads to trineopentylaluminum starting from Me_3Al and isobutene¹³:


$$\text{Cyclopentadiene} + i\text{-Bu}_2\text{AlH} \rightarrow \text{Alkyl-substituted cyclopentadiene} \rightarrow \text{Cyclopentane-1-yl-}i\text{-Bu}_2\text{Al} \quad (\text{g})$$

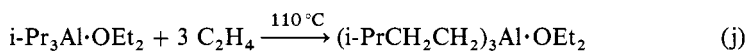
and bicyclic systems¹⁷:



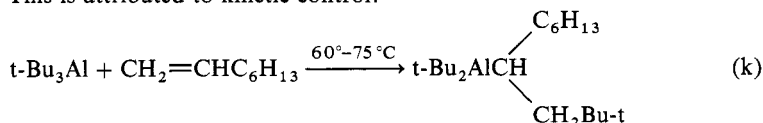
The C—Al bond in $t\text{-Bu}_3\text{Al}$ is active toward ethylene at 20°C and $5\text{--}6 \times 10^6$ Pa (50–60 atm) to give the addition product in high yield:



The ether complex of $t\text{-Bu}_3\text{Al}$ also reacts at $100^\circ\text{--}110^\circ\text{C}$. The mild reaction conditions prevent further addition of the new trialkylaluminum to ethylene¹⁸. Similarly, the ether complex of $i\text{-Pr}_3\text{Al}$ reacts with ethylene at 7×10^6 Pa (70 atm) to give the ether complex of tris(3-methylbutyl)aluminum²⁰:



The additions of C—Al bonds to terminal olefins are regioselective, linking the Al with the terminal carbon atom (>95% terminal C—Al bonds from $n\text{-Pr}_3\text{Al}$ and propene²¹). However, oct-1-ene with $i\text{-Pr}_3\text{Al}$ gives 38:62 terminal to nonterminal C—Al bonds, whereas with $t\text{-Bu}_3\text{Al}$ and oct-1-ene nonterminal C—Al bonds are formed almost exclusively²². This is attributed to kinetic control:

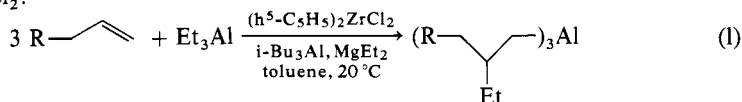


Therefore, the nature of the metal–carbon bond is important for the course of carbometallations²³, and carbalumination in particular.

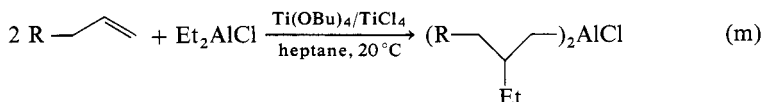
Dialkylaluminum halides, alkoxides, phenoxides and thiolates react with ethylene only in the presence of R_3Al (via alkyl group exchange and growth of the trialkylaluminum)²⁴. The strong association in $\text{R}_2\text{AlNR}'_2$ prevents reaction with ethylene even in the presence²⁴ of R_3Al .

The reaction between triphenylaluminum and olefins requires drastic conditions ($>200^\circ\text{C}$). The hydrocarbons formed by subsequent hydrolysis are 2-phenyloctane (from oct-1-ene), 1,1,2-triphenylethane and triphenylethylene (from $\text{Ph}_2\text{C}=\text{CH}_2$), exo,exo-2,5-diphenylbicyclo[2.2.1]heptane and exo-5-phenylbicyclo[2.2.1]hept-2-ene (from bicyclo[2.2.1]hepta-2,5-diene)²⁵.

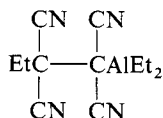
Addition of Et_3Al to terminal alkenes proceeds readily⁴⁷ in the presence of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$:



Similarly, Et_2AlCl adds to terminal alkenes in the presence of Ti(IV) compounds⁴⁷:

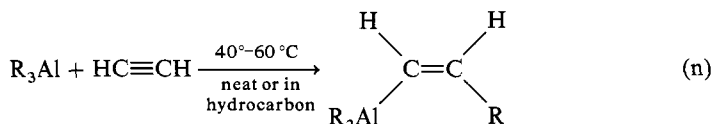


The reaction between AlEt_3 and TCNE proceeds via an intermediate,



to give $\text{EtC(CN)}_2\text{CH(CN)}_2$ after acidic hydrolysis⁴⁸.

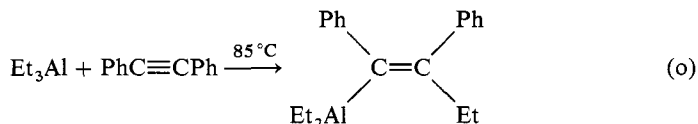
The carbalumination of acetylenes provides a route to alkenylaluminums. The cis addition of R_3Al to $\text{HC}\equiv\text{CH}$ occurs under mild conditions (as compared to the addition to ethylene) for $\text{R} = \text{Et}$ and in particular for $\text{R} = i\text{-Bu}$ ³:



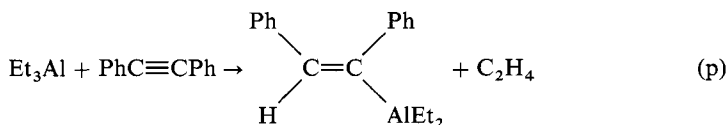
Trimethylaluminum (strongly associated) and dialkylaluminum halides do not react with $\text{HC}\equiv\text{CH}$ under these conditions.

The addition of R_3Al to terminal alkynes requires a higher T. Consequently, metallation of the alkynes (see §5.3.3.5.2) is observed, and only small amounts of addition products (cis and trans) are formed²⁶⁻²⁹.

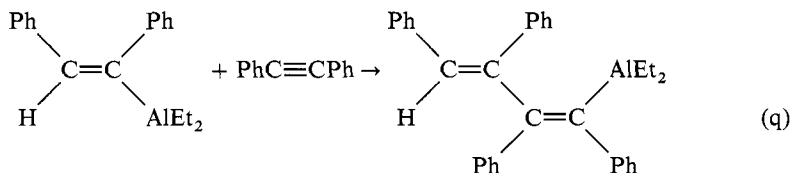
Carbalumination of disubstituted alkynes is even more difficult because it occurs only at high T. This leads to further reactions of the products initially formed³. Thus, treatment of diphenylacetylene with Et_3Al leads to the cis addition product:



The hydrocarbons obtained by hydrolysis of the reaction products show that displacement of ethylene:



and addition of the new alkenylaluminum to $\text{PhC}\equiv\text{CPh}$:

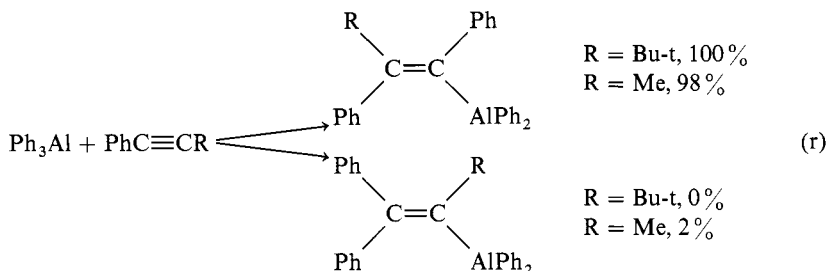


are side reactions³.

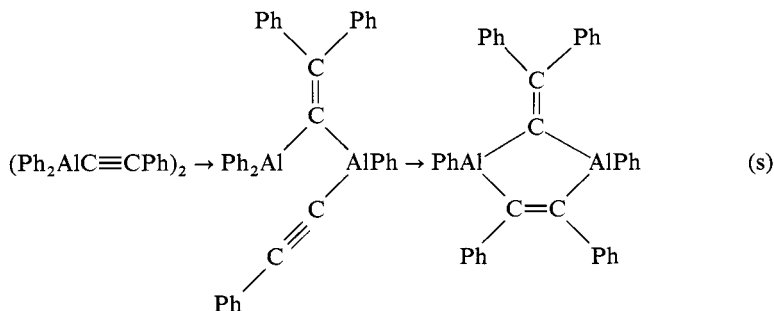
Such reactions as (n) and (o) become predominant when $i\text{-Bu}_3\text{Al}$ is used and the tetraphenylbutadienes are obtained in good yield (75–80%)³. Similarly, the products from such reactions as (m) may enter further carbalumination reactions with the

disubstituted acetylenes, which provides a useful synthesis of pentasubstituted butadienes³.

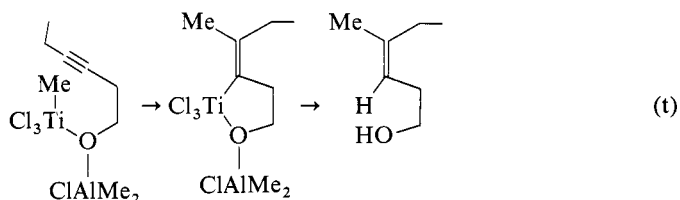
Tribenzyl-³⁰ and triphenylaluminum³¹ give the cis-addition products with $\text{PhC}\equiv\text{CPh}$. With other phenylacetylenes, $\text{PhC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ ³¹, Bu-t ³²) and Ph_3Al regioselective cis addition takes place:



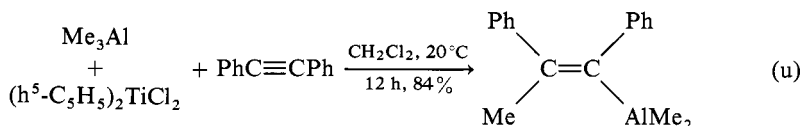
Intramolecular carbalumination of alkynes is observed with the dimeric diphenyl-(phenylethynyl)aluminum. The structures of such compounds^{33,34} are in accord with the assumption of intermediate π -complex formation between the $\text{C}\equiv\text{C}$ bond and Al. Carbalumination is followed by exchange, electrophilic attack at the $\text{C}\equiv\text{C}$ bond and a 1,2 shift of a phenyl group^{33,35}:



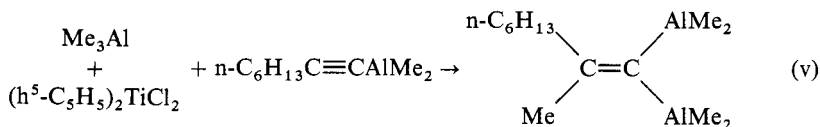
The catalysis of the carbalumination of acetylenes by transition-metal compounds is an attractive target. The presence of Ni ³⁶, Fe ³⁷ or Mn ³⁸ compounds changes the product distribution in the carbalumination of terminal alkynes. However, there is no improvement of the overall stereo- and regiospecificity. The $\text{Me}_3\text{Al}-\text{TiCl}_4$ system leads to carbalumination, but its application is limited owing to low regiospecificity³⁹. Some promising results are attributed to an Al-assisted carbottitanation⁴⁰ rather than to a Ti-assisted carbalumination:



The cis addition of Me_3Al to diphenylacetylene takes place in the presence of 1 equiv $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$, which is superior to the Zr complex⁴¹:

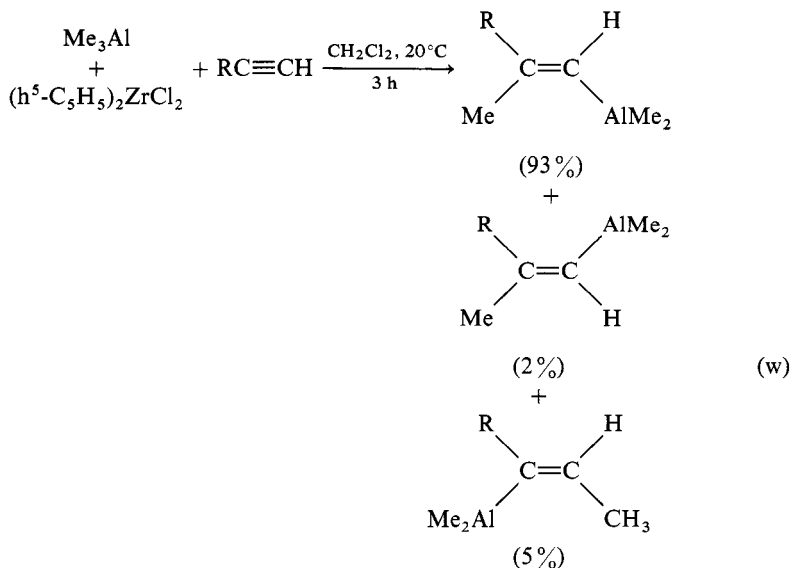


The same carbometallation system affords bis-metallated vinylic species when $\text{Me}_2\text{AlC}\equiv\text{CR}$ is used as the acetylenic component⁴¹:



Instead of Me_3Al , it is possible to use alkylaluminum halides. The carbometallation of $\text{n-C}_6\text{H}_{13}\text{C}\equiv\text{CSiMe}_3$ gives 90% yield of 95:5 cis/trans with the metal linked to C-1.

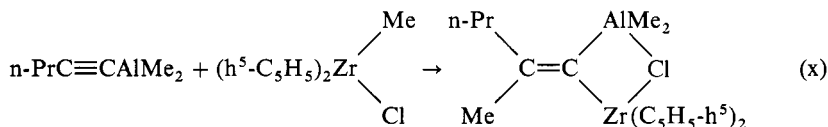
The Me_3Al (xs)– $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ system^{42,43} works an improvement in the carbometallation of terminal alkynes $\text{RC}\equiv\text{CH}$ (R = alkyl, alkenyl, phenyl):



The reaction slows if the Zr complex is not used stoichiometrically. With higher R_3Al (e.g., $\text{n-Pr}_3\text{Al}$), elimination of propene occurs and the alkyne is hydroaluminated or hydrozirconated⁴².

The Me_3Al – $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ carbometallation system is applied equally successfully to functionalized alkynes^{43,44}, tolerating groups Z = OR, SR, I in $\text{Z}(\text{CH}_2)_n\text{C}\equiv\text{CH}$ (n = 1, 2). Because neither Me_3Al nor a preformed reagent, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{ZrMeCl}$, reacts

with terminal alkynes under the conditions, the question arises whether this is an Al-assisted carbozirconation or with a Zr-assisted carbalumination⁴⁵. Although:



is an Al-assisted carbozirconation⁴⁵, there is evidence from other reactions, such as (w), that direct carbalumination takes place, assisted by Zr. This is shown by a low deuterium incorporation (<4%) when the $\text{Me}_3\text{Al-(h}^5\text{-C}_5\text{H}_5)_2\text{ZrCD}_3\text{Cl}$ system is used⁴⁵.

From attempts to use organoaluminum halides to circumvent olefin elimination⁴⁵ and hydrometallation in the presence of Ti or Zr compounds, the use of C—Al bonds in carbometallations may gain importance.

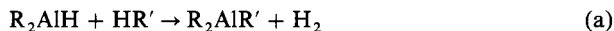
(B. WRACKMEYER)

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5.3.3.5.2. by Substitution of Acidic Carbon—Hydrogen Bonds by Carbon—Al Bonds (Alumination).

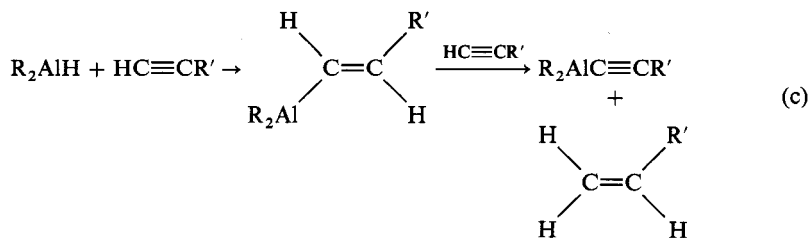
The polarity of Al—H or C—Al bonds is of advantage in alumination reactions. Sufficiently acidic C—H bonds (e.g., in acetylene, cyclopentadienes) can be replaced by new C—Al bonds (e.g., in acetylenes, cyclopentadienes) and then these can be replaced by new C—Al bonds. Direct reaction leads to H₂ evolution:



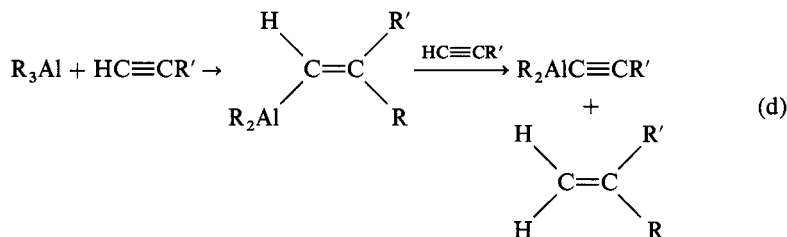
or to formation of a new hydrocarbon:



Alternatively, hydroalumination (see §5.3.3.4.1):



or carbalumination (see §5.3.3.5.1):



e.g., of alkynes, occurs in the first step of the reaction followed by cleavage of the new C—Al bond initially formed. Both direct and indirect alumination are found at the same

5.3. Formation of Bonds

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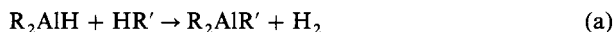
5.3.3. Formation of Carbon—Al Bonds

5.3.3.5. from Other Organoaluminum Compounds

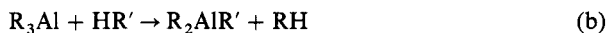
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5.3.3.5.2. by Substitution of Acidic Carbon—Hydrogen Bonds by Carbon—Al Bonds (Alumination).

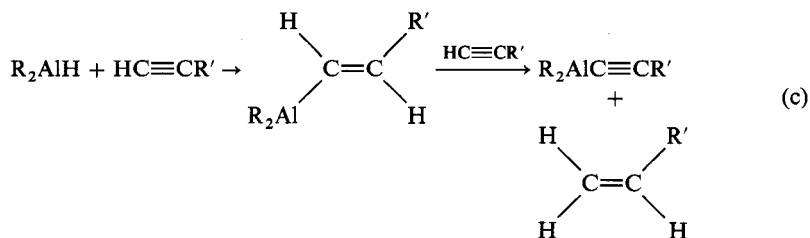
The polarity of Al—H or C—Al bonds is of advantage in alumination reactions. Sufficiently acidic C—H bonds (e.g., in acetylene, cyclopentadienes) can be replaced by new C—Al bonds (e.g., in acetylenes, cyclopentadienes) and then these can be replaced by new C—Al bonds. Direct reaction leads to H₂ evolution:



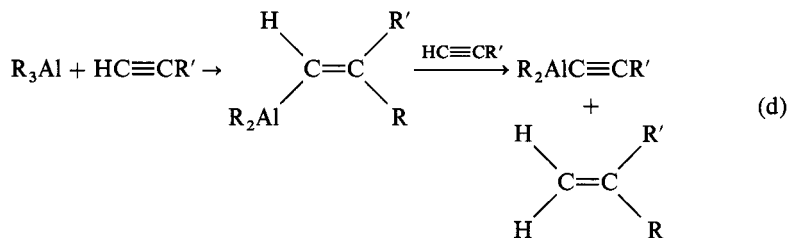
or to formation of a new hydrocarbon:



Alternatively, hydroalumination (see §5.3.3.4.1):



or carbalumination (see §5.3.3.5.1):



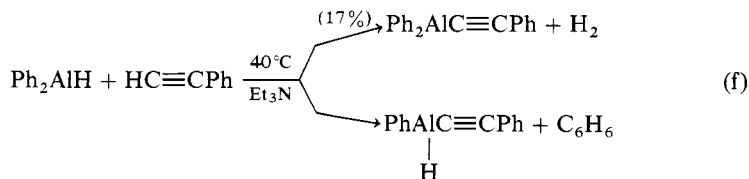
e.g., of alkynes, occurs in the first step of the reaction followed by cleavage of the new C—Al bond initially formed. Both direct and indirect alumination are found at the same

time in one reaction. The reaction conditions determine the relative contributions of Eqs. (a), (c) and Eqs. (b), (d)¹⁻⁴.

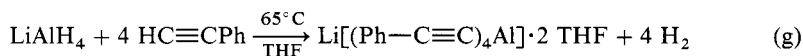
Alumination of terminal acetylenes starting from R_2AlH is best carried out in the presence of tertiary amines. This reduces the rate of hydroalumination, and metallation becomes predominant^{5,6}:



With Ph_2AlH and phenylacetylene, H_2 and benzene (cleavage of $Ph-Al$ bond) result⁷:



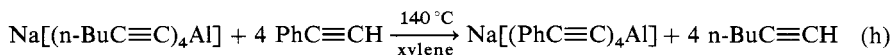
Tetraalkynylaluminates are accessible via the action of terminal alkynes on alkali tetrahydroaluminates. To circumvent hydroalumination, basic solvents are used; secondary amines are catalysts⁸⁻¹⁰:



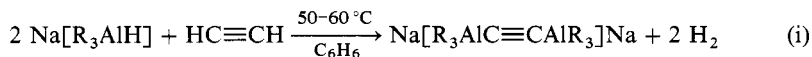
where THF is tetrahydrofuran.

Alkyl halides, R_3Al , R_2AlH or $AlCl_3$ must be absent; otherwise, metallation may be so suppressed that hydroalumination takes place instead.

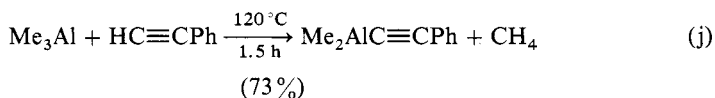
The metallation can be conducted to prepare mono- or dialkynylhydroaluminates (e.g., from hex-1-yne and $Na[AlH_4]$ in THF at $65^\circ C$ or xylene at $140^\circ C$, respectively)¹¹. The different acidity of $C-H$ bonds in terminal acetylenes allows conversion of one tetraalkynylaluminate to another via aluminatation¹¹:



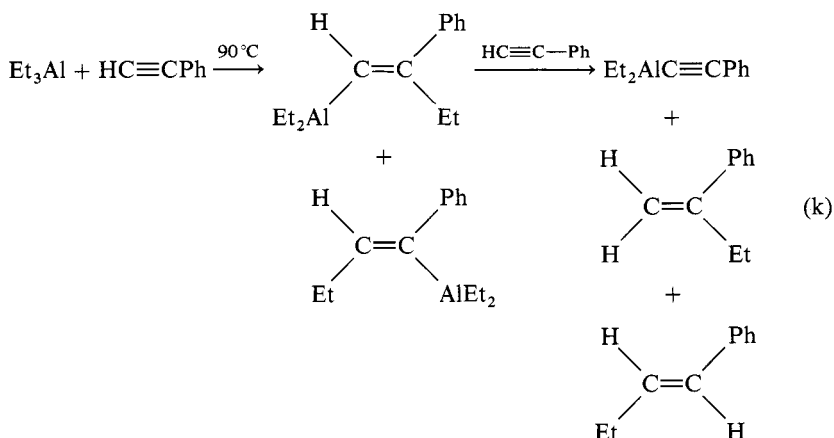
Alkylalkynylaluminates can be obtained from such reactions as (h) when the tetraalkynylaluminate is replaced by a tetraalkylaluminate $[R_4Al]^-$ ($R = Me, Et$)¹¹. However, $140-200^\circ C$ is required. In contrast, the aluminatation of alkynes by $[R_3AlH]^-$ or $[R_2AlH_2]^-$ can be conducted in hydrocarbons under milder conditions^{1,6,10}. The double metallation of acetylene itself by $Na[R_3AlH]$ ($R = C_2H_5, Bu-i$) is quantitative^{1,6}:



Triorganoaluminums react with terminal acetylenes by aluminatation or carbalumination (see §5.3.3.5.1). Direct metallation [see Eq. (a)] of phenylacetylene is the preferred course of reaction for¹² Me_3Al :



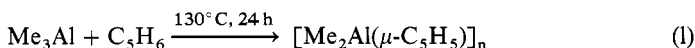
and for^{12,13} Ph_3Al (75–80°C), whereas indirect metallation [see Eq. (d)] dominates¹² for Et_3Al :



$n\text{-Pr}_3\text{Al}$ or $i\text{-Bu}_3\text{Al}$. The indirect reaction becomes less important at RT, when the rate of addition is slow. Excess alkyne also helps to increase the yield, because it compensates for the loss owing to indirect metallation¹⁴.

Although the trialkylaluminum etherates are unreactive toward terminal alkynes, $\text{Et}_3\text{Al}\cdot\text{NEt}_3$ gives⁶ (100–120°C) ethane and $\text{Et}_2\text{AlC}\equiv\text{CR}\cdot\text{NEt}_3$.

The aluminum of cyclopentadiene by R_3Al proceeds only under forcing conditions giving a small yield (e.g., $i\text{-Bu}_2\text{AlC}_5\text{H}_5\cdot\text{h}^1$, 10–20%) and many products from olefin displacement¹⁵. The polymeric compound $[\text{Me}_2\text{Al}(\mu\text{-C}_5\text{H}_5)]_n$ is obtained pure¹⁶:

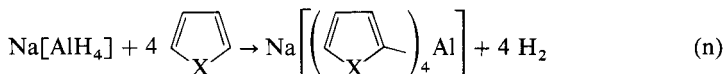


The alkali tetracyclopentadienylaluminates can be prepared from $[\text{AlH}_4]^-$ via aluminatation of cyclopentadiene¹⁷.

Dialkylaluminum cyanides are prepared by aluminatation of HCN starting from^{17,18} R_3Al or²⁰ (less preferably) R_2AlH ($\text{R} = \text{Me}, \text{Et}, \text{Bu-i}$):

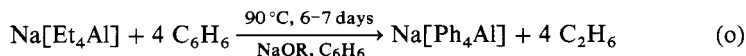


Tetrakis(2-furyl)- and tetrakis(2-thienyl)aluminates can be prepared²¹ by direct substitution of $\text{Na}[\text{AlH}_4]$:



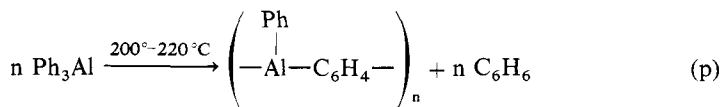
where $\text{X} = \text{O}, \text{S}$.

The aluminatation of benzene is an attractive target because it utilizes the economic synthesis of alkylaluminums (see §5.3.3.2.1) to obtain the less accessible arylaluminums. This is achieved²² by the reaction of $\text{Na}[\text{Et}_4\text{Al}]$ in boiling benzene in the presence of NaOR :

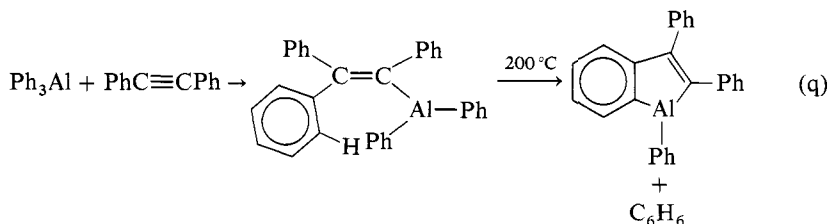


The benzene is metallated by $\text{Na}[\text{Et}]$, which is in equilibrium with $\text{Na}[\text{Et}_3\text{AlOR}]$, $\text{Na}[\text{Et}_4\text{Al}]$ and $\text{Na}[\text{OR}]$. The $\text{Na}[\text{Ph}]$ thus formed may exchange with $\text{Na}[\text{Et}_4\text{Al}]$ or with $\text{Na}[\text{Et}_3\text{AlOR}]$.

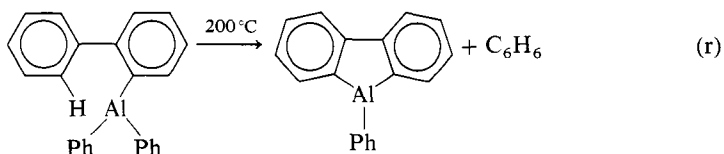
A direct aluminatation of the aryl-H bond takes place²³ in the polymerization of Ph_3Al :



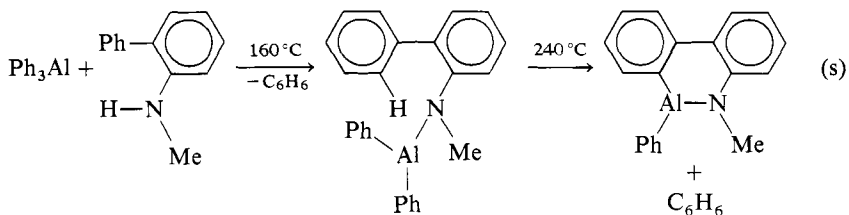
Benzene is also evolved in cyclizations. The carbalumination product of Ph_3Al and diphenylacetylene loses benzene at 200°C , and 1,2,3-triphenyl-1-aluminaindene is obtained²⁴:



The same reaction is used to prepare 9-phenyl-9-aluminafluorene²⁵:



and a heterocycle that contains the Al—N bond, the 9-methyl-10-phenyl-9-aza-10-aluminaphenanthrene²⁶:



(B. WRACKMEYER)

1. H. Lehmkuhl, K. Ziegler, *Aluminium-Organische Verbindungen*, in *Methoden der Organischen Chemie (Houben Weyl)*, E. Müller, ed., Vol. 13/4, Georg Thieme Verlag, Stuttgart, 1970, pp. 75, 153, 160, 171 and 175.
2. T. Mole, E. A. Jeffery, *Organoaluminum Compounds*, Elsevier, Amsterdam, 1972.
3. K. L. Henold, J. P. Oliver, *Organomet. React.* 5, 387 (1975).
4. G. Zweifel, in *Comprehensive Organic Chemistry*, D. Barton and W. D. Ollis, eds., Vol. 3, D. N. Jones, ed. Pergamon Press, Oxford, 1979, p. 1013.
5. V. V. Markova, V. A. Kormer, A. A. Petrov, *J. Gen. Chem. USSR (Engl. Transl.)*, 37, 208 (1967).
6. P. Binger, *Angew. Chem., Int. Ed. Engl.*, 2, 686 (1963).

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16. B. Teclé, P. W. R. Cornfield, J. P. Oliver, *Inorg. Chem.*, **21**, 458 (1982).
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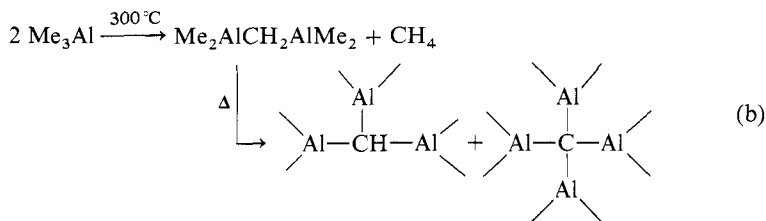
5.3.3.5.3. by Thermal Elimination from R_3Al to Yield Olefin and R'_2Al (Thermal Degradation).

Thermal degradation^{1,2} of R_3Al is involved in the synthesis of R_2AlH , in hydroalumination and in carbalumination (see §5.3.3.2.1, 5.3.3.4.1 and 5.3.3.5.1).

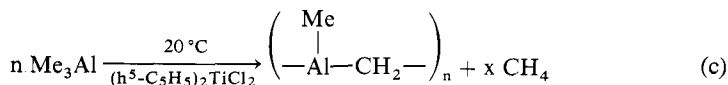
Whenever possible the equilibrium:



its T dependence and the fate of the olefin have to be considered. Heating R_3Al at $>250^\circ C$ leads to decomposition to olefins, alkanes, H_2 and pure Al metal. With Me_3Al , thermal decomposition leads to polymers and finally to Al_4C_3 with CH_4 as the main gaseous product³:



The elimination of CH_4 from Me_3Al is catalyzed by small amounts (1 mol %) of $(h^5-C_5H_5)_2TiCl_2$. This leads to a viscous polymer⁴:



5.3. Formation of Bonds

161

5.3.3. Formation of Carbon—Al Bonds

5.3.3.5. from Other Organoaluminum Compounds

7. J. R. Surtees, *Aust. J. Chem.*, **18** 14(1965).
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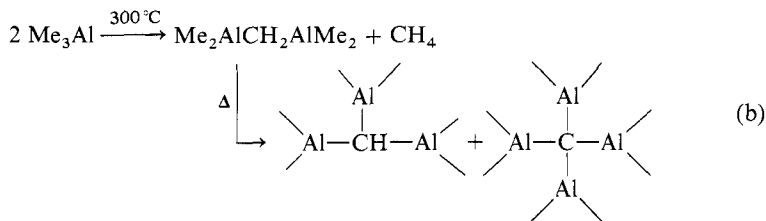
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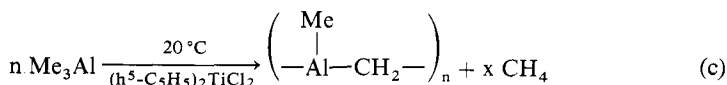
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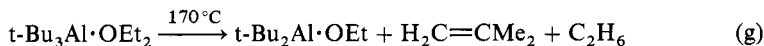
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The elimination of CH_4 from Me_3Al is catalyzed by small amounts (1 mol %) of $(h^5-C_5H_5)_2TiCl_2$. This leads to a viscous polymer⁴:



Trialkylaluminum etherates are less readily isomerized than the ether-free R_3Al . The conditions that lead to olefin elimination cause immediate ether cleavage of the $R_2HAl \cdot O$ complex. This is observed for⁷ $t\text{-Bu}_3Al \cdot OEt_2$:



Thermal elimination of benzene from phenylaluminums is discussed in §5.3.3.5.2.

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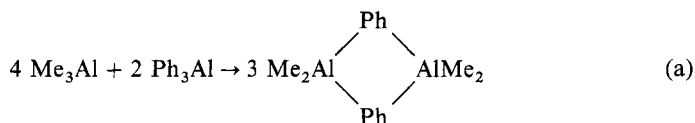
5.3.3.5.4. by Exchange of Organic Groups Between Organoaluminum and Other Organometallics (Transmetallation).

The electron-deficient nature of Al in R_3Al is the driving force for the facile exchange of organic groups¹⁻⁶. The exchange of groups R, R' can occur between R_3Al and AlR'_3 or between R_3Al and other organometallics, MR'_n , leading to new C—Al bonds. The reactions may stop at an intermediate stage, e.g., at complex formation $[MR_3 \cdot AlR'_3]$, or the organoaluminums and the other organometallic species may again dissociate.

In R_3Al , a dimeric structure is observed for groups R with moderate steric requirements (with R = i-Pr, i-Bu, t-Bu the equilibrium is shifted to the monomer).

Rapid scrambling of terminal and bridging alkyl groups, R, takes place in all dimeric compounds, R_3Al , at RT. With R = Me⁷, Et⁸, n-Pr⁸ slow dissociation into monomers followed by rapid reassociation is proposed, whereas for R = cyclopropyl⁹ and p-MeC₆H₄¹⁰ a single bridge-opening process is more likely. The low energy barrier to exchange in R_3Al prevents the preparative use of these exchanges, because even in mixtures of Me_3Al with other R_3Al (the methyl group prefers the bridging position) all alkyl groups exchange rapidly at RT.

The 2:1 reaction between Me_3Al and¹¹ Ph_3Al or¹² $(p\text{-MeC}_6\text{H}_4)_3Al$ leads to quantitative formation of dimeric Me_2AlPh or $Me_2AlC_6H_4Me\text{-}p$, respectively, as crystalline solids that redistribute on distillation¹²:



Similar properties are found¹¹ for Et_2AlPh and $i\text{-Bu}_2AlPh$. Because the thermodynamic stability of R_2AlPh resides in the absence of rapid exchange between terminal and bridging groups; $RAlPh_2$ (R = alkyl) are less stable to redistribution¹¹.

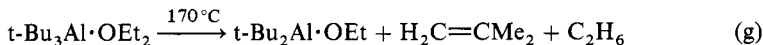
5.3. Formation of Bonds

163

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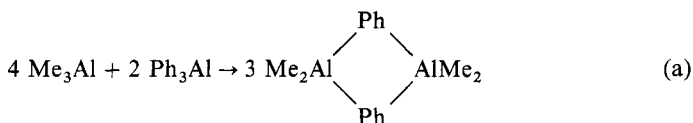
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The 2:1 reaction between Me_3Al and¹¹ Ph_3Al or¹² $(p\text{-MeC}_6\text{H}_4)_3Al$ leads to quantitative formation of dimeric Me_2AlPh or $Me_2AlC_6H_4Me\text{-}p$, respectively, as crystalline solids that redistribute on distillation¹²:



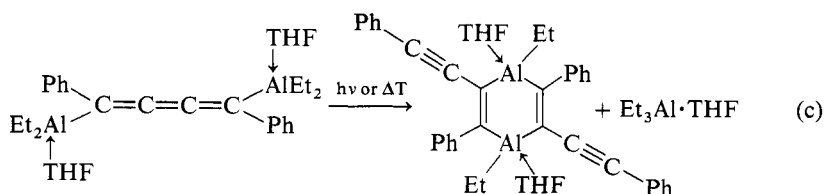
Similar properties are found¹¹ for Et_2AlPh and $i\text{-Bu}_2AlPh$. Because the thermodynamic stability of R_2AlPh resides in the absence of rapid exchange between terminal and bridging groups; $RAlPh_2$ (R = alkyl) are less stable to redistribution¹¹.

The alkynyl group bridges strongly¹⁴. Consequently, $R_2AlC\equiv CR'$ are dimeric and stable. Although the alumination of alkynes (see §5.3.3.5.2) or the reaction between dialkylaluminum halides and metallated alkynes is the preferred method of preparation, disproportionation of R_3Al with $(R'C\equiv C)_3Al$ in ether can also be used¹⁵.

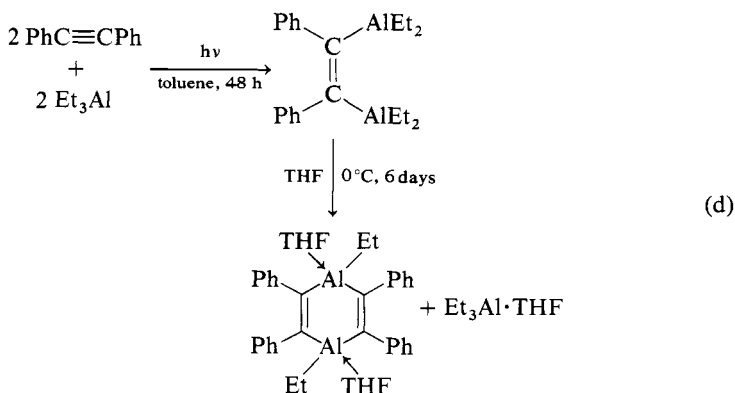
Cyclization of organoaluminums proceeds via intermolecular and intramolecular exchange. The bis-hydroaluminination product of $Me_2AlC\equiv CH$, $(Me_2Al)_3CMe$, can lose Me_3Al leading to a sublimable compound with the composition $Me_6Al_6C_4Me_4$ and an adamantane-like structure¹⁵:



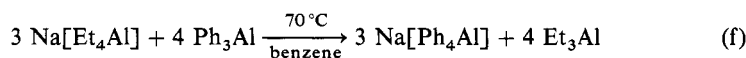
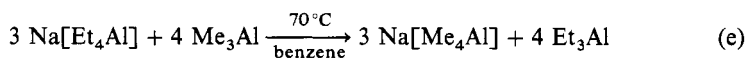
On UV irradiation (20°C) or heating (90°C), a substituted 3-cumulene gives a 1,4-dialuminacyclohexadiene. The $Et_3Al \cdot THF$ (tetrahydrofuran) complex is eliminated¹⁶:



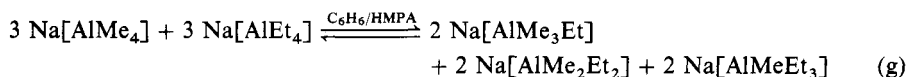
Other 1,4-dialuminacyclohexadienes result from *cis*-dialuminaalkenes^{17,18}. Thus, UV-irradiation of diphenylacetylene and Et_3Al in toluene and addition of THF yields 32% of the bis-THF complex of the heterocycle¹¹⁸:



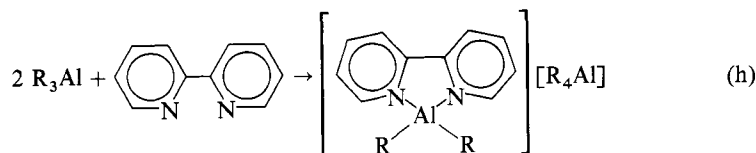
The low solubility of $Na[Me_4Al]$ and $Na[Ph_4Al]$ in benzene allows these aluminates to be prepared from $Na[Et_4Al]$ and Me_3Al and Ph_3Al , respectively³:



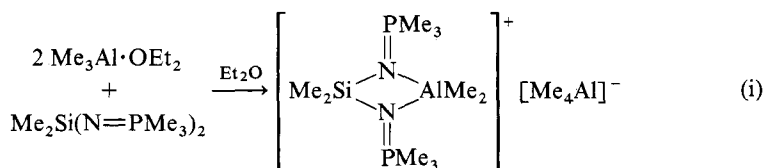
A statistical exchange of alkyl groups occurs with sodium tetraalkylaluminates³⁶:



The exchange of R groups occurs in R_3Al complexes with nitrogen donors. The high conductivity of the adduct of 2,2'-bipyridyl with R_3Al indicates the formation of ionic species¹⁹:



Similarly, autoionization takes place when 2 mol of $Me_3Al \cdot OEt_2$ react²⁰ with $Me_2Si(N=PMe_3)_2$:

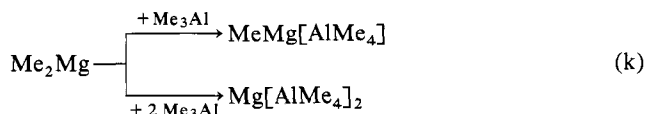


The direct reaction between organoalkali and R_3Al leads to tetraorgano aluminates^{3,4}:



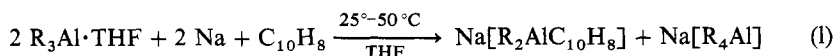
Similar to group-II metal organyls, the reaction is complete with the association of the organometallics. In donor solvents [ether, dimethoxyethane (glyme), etc.] the associates break down to form more definite ionic species, and there is a rapid equilibrium between intimate and solvent-separated ion pairs.

The reaction between Me_2Mg and Me_3Al proceeds according to the stoichiometry employed²:

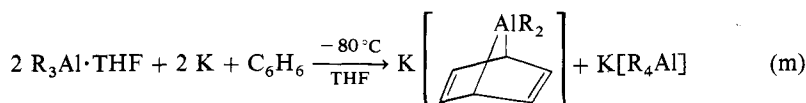


In $Mg[AlMe_4]_2$ the Al and Mg are surrounded by methyl groups²¹. However, there is rapid scrambling of terminal and bridging methyl groups in solution.

Aromatic anions, formed in situ, e.g., by Na and naphthalene, react with R_3Al in THF to form organoaluminates^{22,23}:

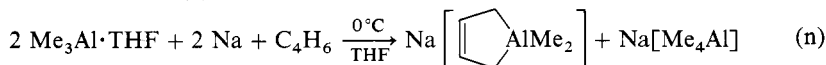


The anion $[Me_2AlC_{10}H_8]^-$ is a dimer²⁴, which may also be true for other analogue anions. Benzene behaves differently (as compared to $C_{10}H_8$, $Me-C_{10}H_7$, anthracene); it does not react with Na, R_3Al , THF, but it reacts²³ in THF with potassium and R_3Al ($R = Me, Et$) at $-80^\circ C$:

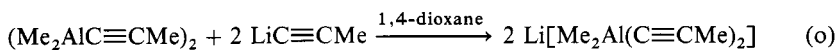


Decomposition of the new aluminate occurs irreversibly above -30°C to give²³ $\text{K}[\text{R}_2\text{PhAlH}]$.

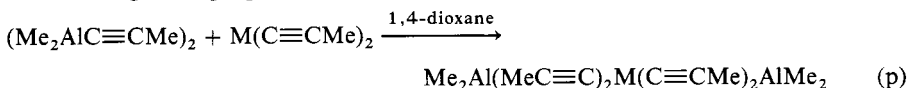
The reaction of conjugated dienes with R_3Al in THF in the presence of alkali metals provides more examples for complex formation between organoalkali and R_3Al . There are differences for various dienes or olefins. With butadiene, Li or Na, Me_3Al the result is reminiscent of reactions (k) and (l)²⁵:



Alkynyllithium or -sodium reacts in 1,4-dioxane with $\text{Me}_2\text{AlC}\equiv\text{CR}$ to give the dimethyldialkynylaluminates. The alkynyl groups show strongly covalent interactions with the alkali metal (even in polar solvents)²⁶. Attempts to prepare dimethyldialkynylaluminates with different alkynyl groups are not successful²⁶.



The reaction between $\text{Me}_2\text{AlC}\equiv\text{CMe}$ and $\text{M}(\text{C}\equiv\text{CMe})_2$ ($\text{M} = \text{Be}, \text{Mg}$) also leads to complexes for which covalent bonding is inferred from low conductance, spectroscopic results and general properties²⁷:

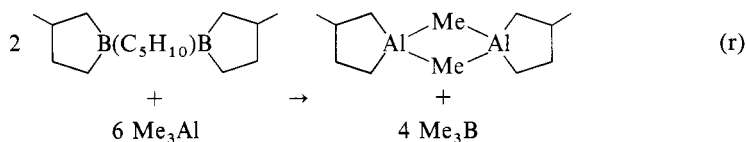


Organoboron compounds form $\text{C}-\text{Al}$ bonds via exchange²⁸. The exchange of organic groups between triorganylborananes and R_3Al or $[\text{R}_4\text{Al}]^-$ occurs. Similarly, $[\text{R}_4\text{B}]^-$ exchange organic groups with R_3Al . The benefit in using organoborananes lies in the volatility of monomeric R_3B , e.g., Me_3B or Et_3B . These R_3B can be removed from the mixture under mild conditions, and the equilibrium can be shifted in the desired direction. Because R_3B can be prepared by straightforward procedures (many of them regio- and stereospecific; see §5.3.2) the conversion of $\text{C}-\text{B}$ to $\text{C}-\text{Al}$ bonds is important in organoaluminum chemistry. Thus, R_3B can be prepared in ethers and the isolation of the ether-free compounds causes no problem. This is in contrast to organoaluminum chemistry because R_3Al form stable complexes with ethers. Exchanges between $\text{R}'_3\text{B}$ and R_3Al are conducted in non-ethers and, therefore, offer a synthesis of ether-free R_3Al . Moreover, Et_3Al , a popular starting material is available commercially. Trimethylaluminum is less reactive (although Me_3B is removed readily) owing to its stronger intermolecular association.

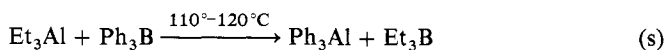
For aliphatic R_3Al , transmetallation is useful in the synthesis of optically active organoaluminums. Mild conditions are required to prevent racemization (see §5.3.3.5.3)³⁰:



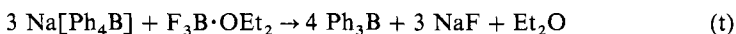
The hydroboration product of isoprene ($2 \text{ BH}_3 + 3 \text{ CH}_2=\text{CMeCH}=\text{CH}_2$) reacts with Me_3Al to give a dimeric cyclic R_3Al that turns to a polymer on heating above 100°C ³¹:



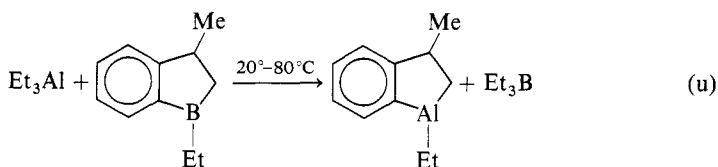
Aryl- or benzylaluminums can be obtained via exchange from the corresponding boron derivatives, which are more easily prepared. Again, the equilibrium is shifted toward the triaryl- or tribenzylaluminum by distilling the Et_3B from the mixture. Quantitative formation of Et_3B is observed^{3,38,29}:



It is often preferable to start from the $[\text{Ph}_4\text{B}]^-$, which are easier to handle. The Ph_3B is set free²⁹ from $[\text{Ph}_4\text{B}]^-$ with $\text{F}_3\text{B} \cdot \text{OEt}_2$:

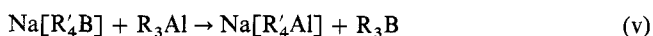


Heterocyclic organoaluminums are prepared by the transmetalation of the corresponding boron compounds²⁸, e.g. for the 3-methyl-1-ethyl-1-aluminaindane^{3,28}:

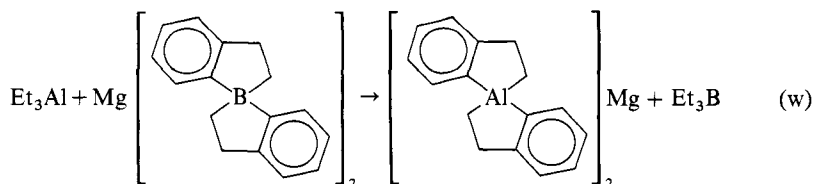


and the method gives 1-alumatetralins^{3,28,31} or 9-aluminafluorenes^{3,28,32}.

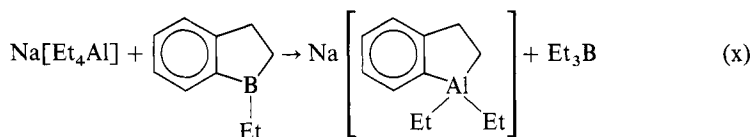
Tetraorganylaluminates are also accessible from the corresponding borates²⁸:



This can be used to prepare spirocyclic aluminates²⁸:



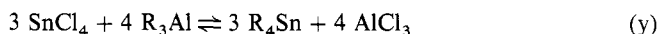
Alternatively, $[\text{Et}_4\text{Al}]^-$ can be used together with 1-ethyl-1-boraindane to prepare a cyclic aluminate²⁸:



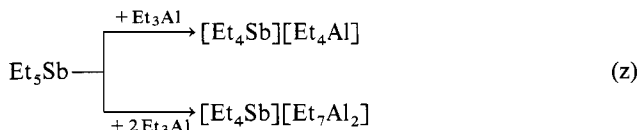
Triorganogalliums exchange organic groups with² R_3Al ; however, this reaction is not used for syntheses. The same applies to organoindiums and -thalliums.

Organometallic group-IV compounds do not yield new C—Al bonds. Alkylaluminums are used as alkylating agents instead; e.g., the SnCl_4 and R_3Al give an equilibrium in

which all possible organotin and aluminums participate³³, in addition to complexes³⁴ between R_2SnCl_2 or R_3SnCl and $AlCl_3$:



The exchange of ethyl groups between Et_3Al and Et_5Sb leads to 1:1 or to 1:2 complexes according to the ratio³⁵:



(B. WRACKMEYER)

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5.3. Formation of Bonds

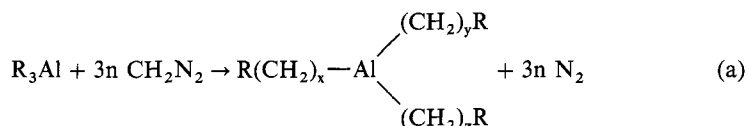
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5.3.3. Formation of Carbon—Al Bonds

5.3.3.5. from Other Organoaluminum Compounds

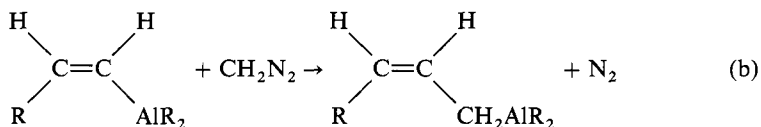
5.3.3.5.5. by Reaction with Diazo Compounds.

The methylene group of diazo compounds inserts into the Al—H^1 , the C—Al^2 and the X—Al bond ($\text{X} = \text{Hal}^{3,4}$ or OR^5) accompanied by N_2 evolution. Insertion into the Al—H or C—Al bond is reminiscent of the growth reaction (see §5.3.3.5.1):



where $x + y + z = 3n$. However, the method is of little importance because a mixture of products is obtained that is more readily available by the well-developed carbalumination of ethylene starting from $^{6,7} \text{Et}_3\text{Al}$ or $n\text{-Pr}_3\text{Al}$.

Diazo compounds insert selectively into the alkenyl C—Al bond⁸, which leads to allylic Al compounds:



After deuteration, DRCHCH=CH_2 is obtained owing to allylic rearrangement.

The reaction between Ph_3Al and diphenyldiazomethane yields a single product, diphenyl(triphenylmethyl)aluminum⁹:



This product proves the existence of the diphenylaluminum radical, which is one of the intermediates formed by thermal decomposition (at $>130^\circ\text{C}$).

A useful reagent results from the reaction^{2,3} of diethylaluminum iodide with CH_2N_2 :



Halomethylaluminum compounds are potential sources of the methylene group.¹⁰

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2. H. Hoberg, *Justus Liebigs Ann. Chem.*, **656**, 1 (1962).
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5.3.4. Formation of Carbon—Ga Bonds

5.3.4.1. from the Elements.

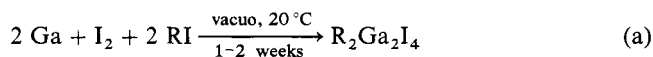
This topic is presented in §5.10.2.

5.3.4.2. from Gallium Metal and Its Alloys

5.3.4.2.1. by the Action of Organic Halides.

Organic halides react with Ga metal slowly. With MeI, $\text{Me}_3\text{Ga}_2\text{I}_3$ can be isolated after 2 weeks shaking at RT. With MeBr, $\text{Me}_3\text{Ga}_2\text{Br}_3$ can be obtained after four weeks¹. In the same way, $\text{Et}_3\text{Ga}_2\text{I}_3$ and $\text{Et}_3\text{Ga}_2\text{Br}_3$ can be prepared¹.

If Ga metal reacts with organic iodides in the presence of I_2 , $\text{R}_2\text{Ga}_2\text{I}_4$ is formed²:



where R = Me, Et, n-Pr, n-Bu.

(L. RÖSCH)

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2. M. Wilkinson, I. J. Worrall, *J. Organomet. Chem.*, **93**, 39 (1975).

5.3.4.2.2. by the Action of Organic Halides on Ga—Mg Alloy or Mixtures of Ga and Mg Metals.

A simple synthesis of R_3Ga is from Ga—Mg alloy or a mixture of these metals with alkyl halides in ethers e.g.¹⁻⁴:

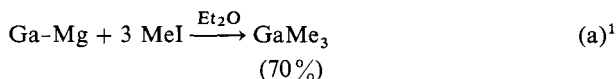


TABLE 1. SYNTHESIS OF ORGANOGALLANES FROM Ga—Mg WITH ORGANIC HALIDES⁵

Organogallane	Alkyl halide	Alloy compos., Ga:Mg	Solvent	Yield (%)
Me_3Ga	MeI	1:3	(i-C ₅ H ₁₁) ₂ O	95
$\text{Me}_3\text{Ga} \cdot \text{OEt}_2$	MeI	1:3	Et_2O	54
$\text{Me}_3\text{Ga} \cdot \text{SEt}_2$	MeI	2:3	Et_2S	41
Et_3Ga	EtBr	2:3	Et_2O	65
$\text{Et}_3\text{Ga} \cdot \text{OEt}_2$	EtBr	2:3	Et_2O	80
(n-Pr) ₃ Ga	n-PrBr	1:3	Et_2S	40
(n-Bu) ₃ Ga	n-BuBr	2:3	n-Bu ₂ O	46
(n-C ₅ H ₁₁) ₃ Ga	n-C ₅ H ₁₁ Br	2:3	PhNMe ₂	42

5.3.4. Formation of Carbon—Ga Bonds

5.3.4.1. from the Elements.

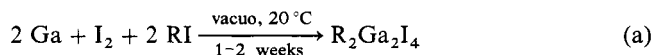
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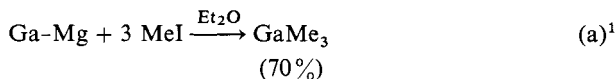


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(n-Bu) ₃ Ga	n-BuBr	2:3	n-Bu ₂ O	46
(n-C ₅ H ₁₁) ₃ Ga	n-C ₅ H ₁₁ Br	2:3	PhNMe ₂	42

This method is improved by using an organic compound containing an electron-donor atom as a catalyst (ethers, sulfides or amines)^{5,6}. These additives serve as initiators. The best yields are obtained using the initiators themselves as solvents. Compounds that are prepared by this method are listed in Table 1. Pure Ga is obtained⁷ from the intermetallic Mg_5Ga_2 .

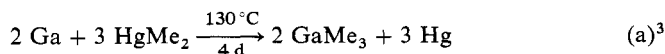
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5.3.4.2.3. by Organomercurials with Ga Metal.

Organomercurials with Ga metal give¹ trialkyl, trialkenyl and triaryl derivatives of Ga¹. A small xs of Ga is taken, and some Hg or HgCl_2 is added.

With HgMe_2 or HgEt_2 , the yields of³ GaMe_3 :



and⁴ GaEt_3 , respectively, are quantitative. Gallium metal and the organomercurial are heated to 100°C or higher for several days. Table 1 lists the compounds synthesized.

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2. E. Wiberg, T. Johannsen, O. Stecher, *Z. Anorg. Allg. Chem.*, 251, 114 (1943).
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5.3. Formation of Bonds

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5.3.4. Formation of Carbon—Ga Bonds

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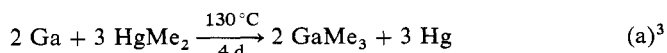
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13. J. R. Manghan, US Pat. 2,969,382 (1961); *Chem. Abstr.*, 55, 11,332 (1961).

TABLE 1. ORGANOGALLANES SYNTHESIZED FROM ORGANOMERCURIALS WITH Ga METAL

Organogallane	Yield (%)	Ref.
Me ₃ Ga	100	2,4
Et ₃ Ga	100	3
n-Pr ₃ Ga	80	5
i-Pr ₃ Ga	75	5
[CH ₂ (c-C ₅ H ₉)] ₃ Ga	^a	6
(C ₂ H ₅) ₃ Ga	40	7
(C ₃ H ₇) ₃ Ga	87	5
[(CH ₂) ₄ CH=CH ₂] ₃ Ga	^a	8
(c-C ₃ H ₅) ₃ Ga	^a	9
Ph ₃ Ga	82,88	10,11
(2-CH ₃ C ₆ H ₄) ₃ Ga	89	11
(3-CH ₃ C ₆ H ₄) ₃ Ga	49	11
(4-CH ₃ C ₆ H ₄) ₃ Ge	92	11
(4-EtC ₆ H ₄) ₃ Ga	58	11
(4-Me ₃ CC ₆ H ₄) ₃ Ga	84	11
(4-MeOC ₆ H ₄) ₃ Ga	73	11
(3-FC ₆ H ₄) ₃ Ga	80	11
(4-FC ₆ H ₄) ₃ Ga	98	11
(2-ClC ₆ H ₄) ₃ Ga	65	11
(3-ClC ₆ H ₄) ₃ Ga	59	11
(4-ClC ₆ H ₄) ₃ Ga	40	11
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(2,4,6-Me ₃ C ₆ H ₂) ₃ Ga	8	12
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Electrolysis of AlEt₃ or other R₃Al in a conducting medium with exclusion of air and moisture using a Ga anode delivers alkylgallanes^{1,2}. Metal alkyls other than Al alkyls can also be employed^{1,3}.

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Me_3Ga , which is the primary product of the electrode reaction. When EtI or $\text{ICH}_2\text{CH}_2\text{CN}$ is used instead, no definite Ga compound can be isolated¹.

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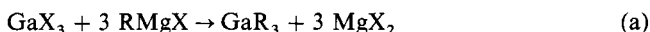
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5.3.4.3. from Ga or Organogallium Halides

5.3.4.3.1. with Other Organometallics.

(i) With a More Polar Organometallic. This is not an important method for gallanes; these can be better obtained from Ga metal and a diorganomercurial because of the stable 1:1 adducts formed with the basic solvents used [e.g., ether, tetrahydrofuran (THF)]. However, Ga trihalides, GaX_3 , can be alkylated and arylated by organometallics.

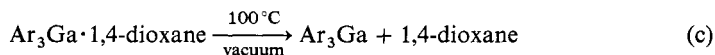
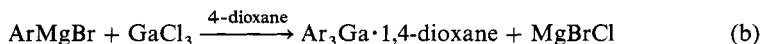
Organomagnesium halide reagents react with GaX_3 to give, depending on the conditions, 1:1 solvates or solvent-free R_3Ga :



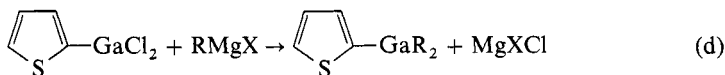
Likewise, $\text{GaMe}_3 \cdot \text{OEt}_2$ is prepared¹ by adding GaBr_3 in ether to EtMgBr in ether under N_2 . The exothermic reaction maintains reflux. The mixture is fractionated at low T under vacuum. Similarly, but with the solvent distilled at atm P, the etherate $\text{Me}_3\text{Ga} \cdot \text{OEt}_2$ is obtained² as a stable liquid (99°C, 762 torr).

The reaction of GaCl_3 and MeMgI in ether must be refluxed 40 h. The etherate is isolated³ by distillation at 50 torr and purified by distillation (bp 98.3°C; mp -76°C). It should be possible to obtain solvent-free compounds by replacing ether by high-boiling alkyl oxides. However, for $n\text{-PrMgCl}$ in Et_2O , the etherate is obtained if the solvent is evaporated under vacuum⁴ and free $n\text{-Pr}_3\text{Ga}$ (bp 184°C) is produced if it is distilled at atm P. The same applies⁵ to Et_3Ga , $(n\text{-Bu})_3\text{Ga}$, $(i\text{-Pr})_3\text{Ga}$ and $(i\text{-Bu})_3\text{Ga}$.

Attempts to prepare $(\text{Vy})_3\text{Ga}$ from VyMgCl (Vy = vinyl) fail⁶. When working with aryl or higher alkyl derivatives, the etherates are obtained by the organomagnesium-halide route, but the etherate dissociates on vacuum distillation. Ring-substituted Ph_3Ga are obtained⁷:



A similar procedure yields $(t\text{-Bu})_3\text{Ga}$ from $t\text{-BuMgCl}$ and GaBr_3 in ether⁸, and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ is also prepared from GaCl_3 and $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in ether in 92% yield⁹. The best conditions involve 13% xs organomagnesium halide reagent. This route is employed¹⁰ to prepare $(\text{C}_6\text{F}_5)_3\text{Ga} \cdot \text{OEt}_2$. Mixed 2-thienyldialkylgallane are prepared¹¹ by reacting 2-thienylgallium dichloride with RMgX derivatives.



To avoid etherate formation more reactive organometallics are used.

5.3. Formation of Bonds

173

5.3.4. Formation of Carbon—Ga Bonds

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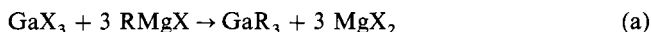
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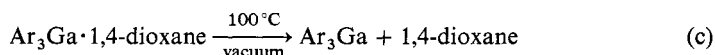
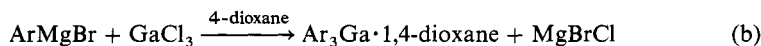
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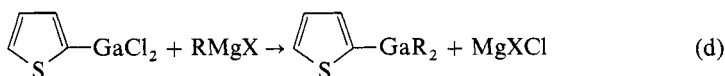
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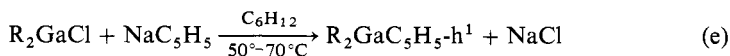


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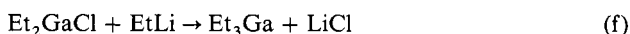
Vinylsodium fails to yield Vy_3Ga , but the method works¹² with cyclopentadienyl and acetylenic derivatives:



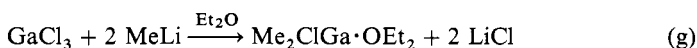
Dialkylgallium cyclopentadienyl derivatives are obtained ($R = Me$, mp $68^\circ-69^\circ C$; Et , mp $36^\circ-37^\circ C$).

Dimethylpropinylgallium¹³ is prepared in 40–60% yield. It is a colorless solid (mp $50-51^\circ C$), dimeric in solution, which can be purified by sublimation (50° , 0.1 torr), and is soluble in organic solvents. In ether a 1:1 adduct is partially formed. Protic acids specifically cleave the propinyl group.

Lithium alkyls are used in halogen-alkyl exchange with Ga halides, e.g.¹⁴:



and $Me_2ClGa \cdot OEt_2$ prepared¹⁵ by adding 2 mol of $MeLi$ to $GaCl_3$ in ether:



Likewise, $GaMe_3$ is obtained¹⁶ as intermediate in the preparation of $(Me_2GaOH)_3$.

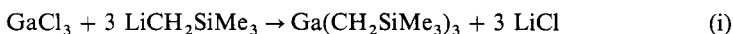
This method^{17,18} allows base-free R_nGaCl_{3-n} to be prepared where $R = n-Bu$ and $n = 1-3$. The synthesis involves the metathesis of RLi with $GaCl_3$ in hydrocarbons and proceeds stoichiometrically. The ratio of RLi and $GaCl_3$ must be controlled:



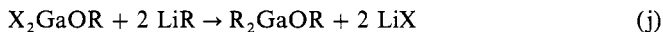
Tri-*n*-butylgallium is prepared in 90–97% yields by dropwise addition of 3:1 *n*-BuLi in benzene to $GaCl_3$ in benzene and heating at reflux. The workup involves filtering the $LiCl$, removing the solvent in vacuo at RT and vacuum fractionation.

The procedure is generalized to $R = Et$, *n*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, *t*-Bu and vinyl compounds. Benzene is the best solvent. Completing the reaction requires heating at $70^\circ C$ for 12 h. Excess RLi gives $LiGaR_4$.

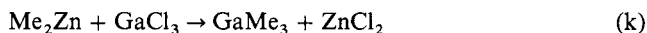
The same technique applies¹⁹ to $Ga(CH_2SiMe_3)_3$ from $GaCl_3$ and $LiCH_2SiMe_3$:



Dialkylalkoxygallanes can be obtained from alkyldihalogenogallanes with RLi :



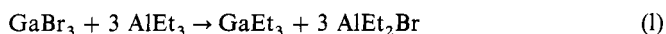
Unsolvated Me_3Ga can be obtained in 90% yield by reacting GaX_3 with Me_2Zn vapor³:



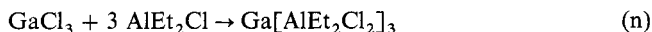
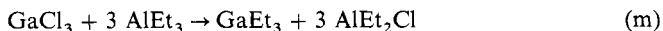
The reaction starts vigorously and is controlled by the rate of flow of the vapor but requires $80^\circ-120^\circ C$ for completion.

Aluminum alkyls are used to obtain $GaMe_3$ ²⁰ and unsolvated $GaEt_3$ ²¹.

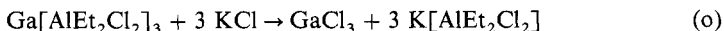
Good results are obtained²² when only one alkyl group is available for alkylation. With $GaBr_3$ and Et_3Al the yield is $>80\%$:



With GaCl_3 , however, the yield is only 45% owing to the formation of a stable complex:



However, if xs KCl is added to the medium, an additional 42% yield of GaEt_3 is obtained owing to the displacement of GaCl_3 from the Al complex:



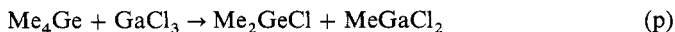
and $i\text{-Bu}_3\text{Ga}$ is obtained similarly in 90% yield. Also, Me_3Ga can be obtained in 90–93% yield from²³ GaBr_3 with Me_2AlBr without solvent followed by dropwise addition of stoichiometric Me_3Al . The mixture reaches 140°C , and Me_3Ga distills.

(ii) With a Less Polar Organometallic. One Si—C bond of Me_4Si can be split by GaCl_3 to give MeGaCl_2 , and the reaction can be extended to higher alkyl derivatives²⁴. The reaction works with GaBr_3 but not with GaI_3 . From SiEt_4 , EtGaX_2 $\text{X} = \text{Cl}, \text{Br}$ is obtained in 94 (84)% yield²⁵.

With unsymmetrical tetraalkylsilanes some selectivity appears; e.g., Me_3EtSi with GaCl_3 gives MeGaCl_2 and Me_2EtSiCl , but only traces of EtGaCl_2 and Me_3SiCl . With GaBr_3 the possible products are obtained statistically.

From $\text{Me}_3\text{SiCH}_2\text{Cl}$ and GaCl_3 only $\text{ClCH}_2\text{GaCl}_2$ and Me_3SiCl are obtained, and Me_3SiPh leads almost specifically to PhGaCl_2 and Me_3SiCl ; Me_3SiV reacts with GaCl_3 to give a mixture of Me and VyGaCl_2 .

The mechanism involves electrophilic attack of the GaCl_3 electron-pair acceptor acid on a carbon atom vicinal to Si, leading to cleavage of the Si—C bond by a four-centered transition state. Tetramethylgermane reacts like SiMe_4 , but the Ge—C bond is weaker than the Si—C bond, and the reaction proceeds at RT to MeGaCl_2 :



However, Me_4Sn reacts even at 0°C with GaCl_3 exothermically to produce Me_3SnCl and MeGaCl_2 as a 1:1 adduct²⁶:



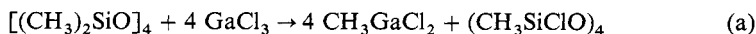
(J. C. MAIRE)

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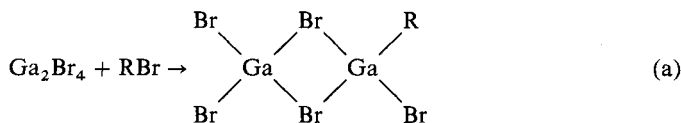
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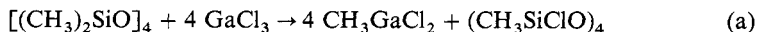
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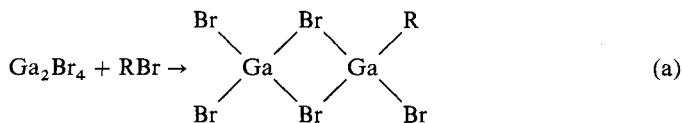
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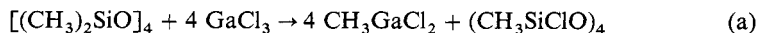
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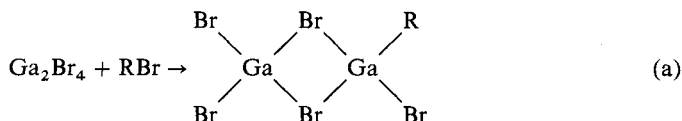
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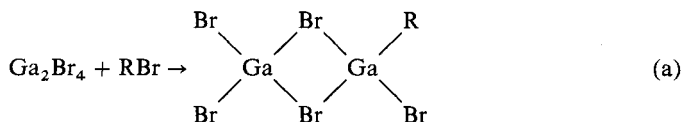
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Trimethylsilyl-methylhalogenogallane derivatives, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_n\text{X}_{3-n}$, are obtained by redistribution³; e.g., $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Br}_2$, $\text{Ga}(\text{CH}_2\text{SiMe}_3)\text{Cl}_2$ and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ are prepared from GaR_3 and HCl . The procedure involves adding R_3Ga in benzene to GaCl_3 in benzene at 25°C for 12 h. The above compounds are dimeric in benzene (cryoscopy).

Redistribution is used to prepare arylgallium halides. The complete series, $\text{Ph}_n\text{GaX}_{3-n}$, $n = 1, 2$ for $\text{X} = \text{Cl}, \text{Br}, \text{I}$, is known² (GaCl_3 is more reactive than GaBr_3).

The conditions can be summarized:

Ph_2GaCl	$\text{Ph}_3\text{Ga}, \text{GaCl}_3$ (2:1)	$150^\circ\text{C}, 12\text{ h}$
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PhGaI_2	$\text{Ph}_3\text{Ga}, \text{GaI}_3$ (1:2)	benzene reflux, 12 h

The Ph_2GaI is prepared from Ph_3Ga by bromine elimination. The products are dimers in the solid and in benzene. Molten PhGaCl_2 is conductive.

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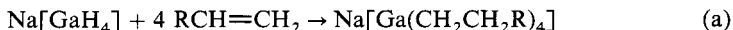
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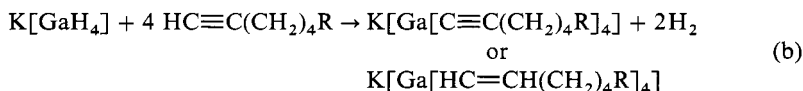
Only coordination complexes of GaH_3 with organic bases; such as Me_3N , Me_2NH , Me_2Ph , are known¹. The synthetic possibilities are not investigated. The products are insoluble in hydrocarbons and decompose at RT in ether.

Although GaH_3 does not exist, mixed hydrides, MGaH_4 , are known with $\text{M} = \text{Li}$, Na , K , Rb and Cs . These products are reagents for organic reactions; e.g., $\text{Na}[\text{GaH}_4]$ adds to olefinic double bonds²:



where $\text{R} = \text{n-C}_4\text{H}_9$, $\text{n-C}_5\text{H}_{11}$, $\text{n-C}_6\text{H}_{13}$. The reaction proceeds at $50^\circ\text{--}60^\circ\text{C}$ in 85–95 % yield. Partial isomerization of the α -olefins is observed. Adding Br_2 to the mixture furnishes $\text{BrCH}_2\text{CH}_2\text{R}$. The reaction is catalyzed by $\text{h}^5\text{-C}_5\text{H}_5\text{TiCl}_2\text{-Na}[\text{AlEt}_4]$.

Potassium and Na tetrahydrogallate react with terminal alkynes³ either (1) by metallation to give tetraalkynylgallates, or (2) by addition to give tetraalkenylgallates:



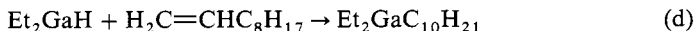
The influence of the conditions is decisive. With $\text{R} = \text{H}$, CH_3 or Et metallation predominates. However, with $\text{R} = \text{C}_6\text{H}_5$ in diethyleneglycol dimethyl ether (diglyme) or tetrahydrofuran (THF), addition is preferred.

Alkylgallium hydrides are also often obtained as complexes with nitrogen bases; e.g.⁴, $\text{Me}_3\text{N}\cdot\text{GaH}_2\text{Me}$ is obtained from $\text{Me}_3\text{N}\cdot\text{GaH}_3$ by reaction with HgMe_2 , $\text{Me}_3\text{N}\cdot\text{GaMe}_2\text{H}$ is obtained from $\text{Me}_3\text{N}\cdot\text{GaMe}_3$ and LiH , $\text{Me}_3\text{N}\cdot\text{GaH}_2\text{Me}$ is obtained from $\text{Me}_3\text{N}\cdot\text{GaH}_2\text{Cl}$ and MeLi and $\text{Me}_3\text{N}\cdot\text{GaHMe}_2$ are obtained from $\text{Me}_3\text{N}\cdot\text{GaH}_3$ and $\text{Me}_3\text{N}\cdot\text{GaMe}_3$. The latter redistribution method can be used to prepare deuterated compounds, such as $\text{Me}_3\text{N}\cdot\text{GaDMe}_2$, from $\text{Me}_3\text{N}\cdot\text{GaD}_3$ and $\text{Me}_3\text{N}\cdot\text{GaMe}_3$ (the same for $\text{Me}_3\text{N}\cdot\text{GaD}_2\text{Me}$).

Few solvent-free alkylgallium hydrides are known, but hydride intermediates appear more often. The best known is Et_2GaH , obtained in only 25–30 % yield by:



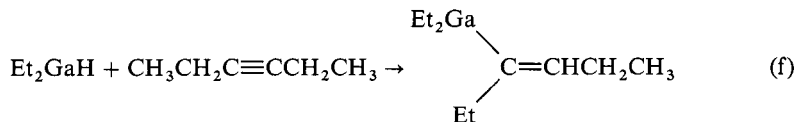
The product can be obtained in 95 % purity; **it flames spontaneously in air**, reacts vigorously with H_2O and decomposes at $>80^\circ\text{C}$; Et_2GaH is similar to Et_2AlH in that it reacts with α -olefins⁵ at moderate T. The reaction with 1-decene proceeds at 65°C leading to a product resulting from the addition of the hydrogen to the carbon bearing the fewest hydrogens:



but at 100°C the product disproportionates:



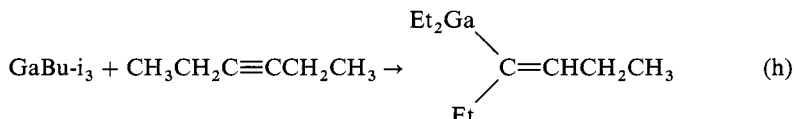
Similarly, 3-hexyne under the same conditions react to form:



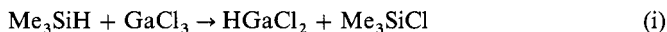
These reactions can lead to unsymmetrical $\text{GaR}_2\text{R}'$. Dialkylgallium hydrides can be generated in situ by thermal elimination of an olefin from a suitable GaR_3 ; e.g., GaBu_3 -i reacts⁵ with α -olefins to yield isobutylene and $\text{GaR}_2\text{CH}_2\text{CH}_2\text{R}'$:



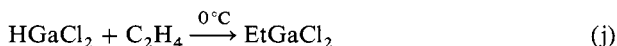
at $150^\circ\text{--}160^\circ\text{C}$. With 3-hexyne at 140°C , the same reaction furnishes the diethylgallio olefin and isobutylene:



Although GaH_3 is not known, HGaCl_2 is obtained⁶ from GaCl_3 and Me_3SiH at -30°C . The HGaCl_2 can be isolated in high yield⁷ by vacuum distillation, but it is easier to do a one-step reaction in which the mixture obtained from:



is used directly, e.g., to absorb C_2H_4 :



With propylene the reaction is not so clean because propylene polymerizes more easily than ethylene; however, if a slurry of HGaCl_2 in pet. ether is used, n-PrGaCl_2 is obtained in 85–90% yield, but no i-PrGaCl_2 . This establishes that hydrogen added to the carbon with less hydrogen.

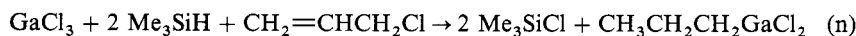
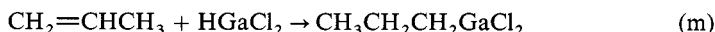
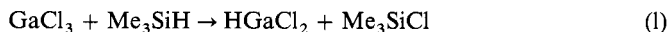
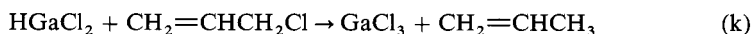
With n-heptene under the same conditions, n-heptyl-GaCl_2 is obtained in 90% yield. At $0^\circ\text{--}5^\circ\text{C}$, cyclohexene gives an exotherm, which furnishes cyclohexyl- GaCl_2 quantitatively. At lower T no reaction takes place. The reactivity order is, therefore, the same as for hydroalanaion, but the reaction is easier.

The bromide HGaBr_2 is less stable than HGaCl_2 (it decomposes at $> -5^\circ\text{C}$), but leads to the same reactions. However, yields are lower owing to more effective catalysis of the polymerization.

Defined products cannot be isolated from the polymeric mixture resulting from HGaCl_2 with 2,3-dimethylbutadiene-1,3, and the same is true with styrene.

By passing dry acetylene through a suspension of HGaCl_2 in pet. ether, white crystalline $\text{GaCl}_2\text{CH}_2\text{CH}_2\text{GaCl}_2$ is obtained⁷.

Starting from phenylacetylene, only polymers are observed. Allyl chloride undergoes halogen-hydride exchange as well as addition to the double bond. The final product is n-PrGaCl_2 , obtained in 83% yield (estimated after transformation into n-PrI). The corresponding equations are:



where HGaCl_2 can be a precursor for alkylgallium hydrides. Reacting its Me_3N adduct with MeLi gives the corresponding adduct of dimethylgallium hydride⁴:



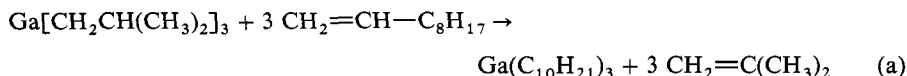
Similarly, $\text{Me}_3\text{N} \cdot \text{GaH}_2\text{Me}$ can be prepared from $\text{Me}_3\text{N} \cdot \text{GaH}_2\text{Cl}$, obtained from $\text{Me}_3\text{N} \cdot \text{GaMe}_2\text{Cl}$ and LiH .

(J. C. MAIRE)

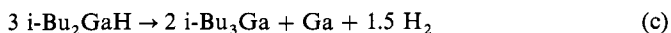
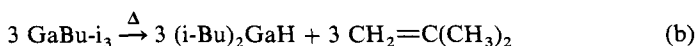
1. N. N. Greenwood, E. J. F. Ross, A. Storr, *J. Chem. Soc., A*, 706 (1966).
2. V. V. Gavrilenko, V. S. Kolesov, L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 960 (1980).
3. V. V. Gavrilenko, V. S. Kolesov, Yu. N. Smirnov, L. I. Zakharkin, *J. Gen. Chem. USSR (Engl. Transl.)*, 48, 2067 (1978).
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6. H. Schmidbaur, W. Findeiss, E. Gast, *Angew. Chem. Int. Ed. Engl.*, 77, 170 (1965).
7. H. Schmidbaur, H. F. Klein, *Chem. Ber.*, 100, 1129 (1967).

5.3.4.4.2. by Transfer of Ga Hydride from One Olefin to Another: Alkylgallium—Olefin Displacement.

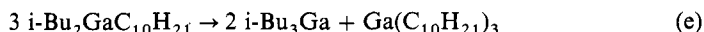
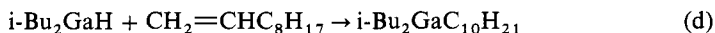
Heating $i\text{-Bu}_3\text{Ga}$ with xs 1-decene evolves isobutylene at $155^\circ\text{--}160^\circ\text{C}$. Pumping off xs decene leaves pure $n\text{-decyl}_3\text{Ga}$:



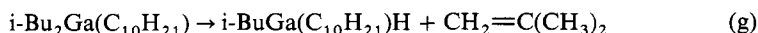
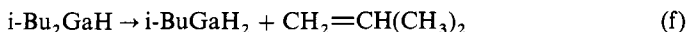
This is an excellent route to high mol wt, nondistillable Ga alkyls. The mechanism is revealed by the thermal decomposition of $i\text{-Bu}_3\text{Ga}$. At 155°C , isobutylene and H_2 form in a ca. 2:1 ratio, corresponding to:



With olefin, $i\text{-Bu}_2\text{GaH}$ adds immediately, and the unsymmetrical $\text{R}_2\text{GaR}'$ obtained disproportionates to give:



This scheme agrees with the reaction above, i.e., the addition of Et_2GaH to 1-decene, and is preferred to the stepwise elimination of isobutylene:



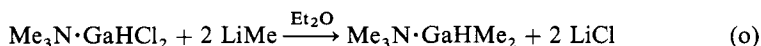
The mechanism is found from the kinetics¹ of the gas-phase intramolecular elimination of isobutene from $i\text{-Bu}_3\text{Ga}$ with xs ethylene at 416–500 K. The primary

5.3. Formation of Bonds

5.3.4. Formation of Carbon—Ga Bonds

5.3.4.4. from Ga Hydrides or Organogallium Hydrides

where HGaCl_2 can be a precursor for alkylgallium hydrides. Reacting its Me_3N adduct with MeLi gives the corresponding adduct of dimethylgallium hydride⁴:



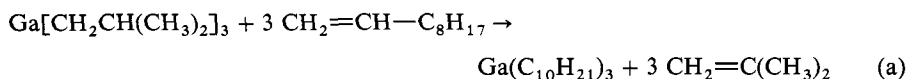
Similarly, $\text{Me}_3\text{N} \cdot \text{GaH}_2\text{Me}$ can be prepared from $\text{Me}_3\text{N} \cdot \text{GaH}_2\text{Cl}$, obtained from $\text{Me}_3\text{N} \cdot \text{GaMe}_2\text{Cl}$ and LiH .

(J. C. MAIRE)

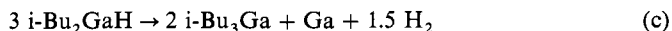
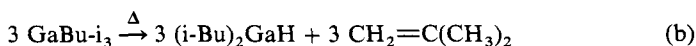
1. N. N. Greenwood, E. J. F. Ross, A. Storr, *J. Chem. Soc., A*, 706 (1966).
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5.3.4.4.2. by Transfer of Ga Hydride from One Olefin to Another: Alkylgallium—Olefin Displacement.

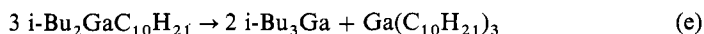
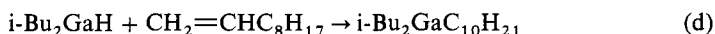
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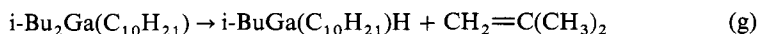
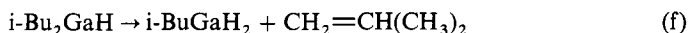
This is an excellent route to high mol wt, nondistillable Ga alkyls. The mechanism is revealed by the thermal decomposition of $i\text{-Bu}_3\text{Ga}$. At 155°C, isobutylene and H_2 form in a ca. 2:1 ratio, corresponding to:



With olefin, $i\text{-Bu}_2\text{GaH}$ adds immediately, and the unsymmetrical $\text{R}_2\text{GaR}'$ obtained disproportionates to give:

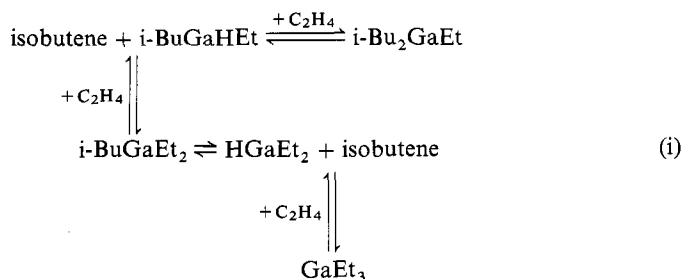
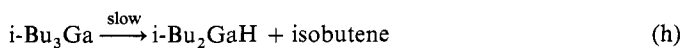


This scheme agrees with the reaction above, i.e., the addition of Et_2GaH to 1-decene, and is preferred to the stepwise elimination of isobutylene:



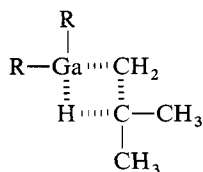
The mechanism is found from the kinetics¹ of the gas-phase intramolecular elimination of isobutene from $i\text{-Bu}_3\text{Ga}$ with xs ethylene at 416–500 K. The primary

reaction product $i\text{-Bu}_2\text{GaH}$, is thermodynamically unstable and adds to ethylene to form the mixed trialkylgallium, $i\text{-Bu}_2\text{GaEt}$. The overall pathway is:



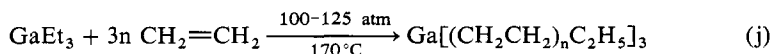
The rate-determining step is (h), and the three dissociation steps are kinetically similar.

The results are interpreted in terms of a tight, cyclic-4-centered transition state such as:



The concerted mechanism accounts for the small influence of R on the elimination rate.

With unbranched Ga alkyls polymerization is observed² at ca 10^7 Pa:



Although similar, the reaction is more difficult than for Et_3Al .

With GaMe_3 no olefin can be formed. Insertion³ of GaMe_3 , observed with 2,3-dicarba-nido-hexaborane(8) gives 1-methyl-1-galla-2,3-dicarba-closo-hexaborane(7), (Fig. 1) in which Ga is incorporated into a closed polyhedral system. The reaction proceeds at 215°C in the gas phase. The insertion can be observed⁴ with GaEt_3 , and from (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{13}$, 7,8- μ -diethylgallo-1,2-dicarba-nido-undecaborane(13) is obtained. By further heating in benzene, two Ga—C bonds are created by thermal closing of the icosahedral skeleton to produce 3-ethyl-3-gallo-1,2 dicarba-closo-dodecaborane(12). (Fig. 2).

(J. C. MAIRE)

1. K. W. Egger, *J. Chem. Soc., A*, 3604 (1971).

2. J. J. Eisch, *J. Am. Chem. Soc.*, **84**, 3830 (1962).

3. D. A. T. Young, R. J. Wiersema, M. F. Hawthorne, *J. Am. Chem. Soc.*, **93**, 5687 (1971).

4. R. N. Grimes, W. J. Rademaker, *J. Am. Chem. Soc.*, **94**, 1864 (1972).

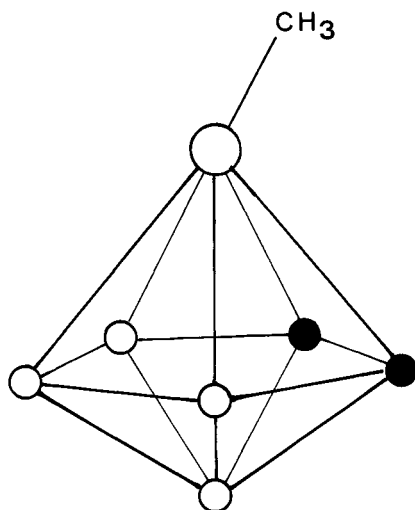


Figure 1.

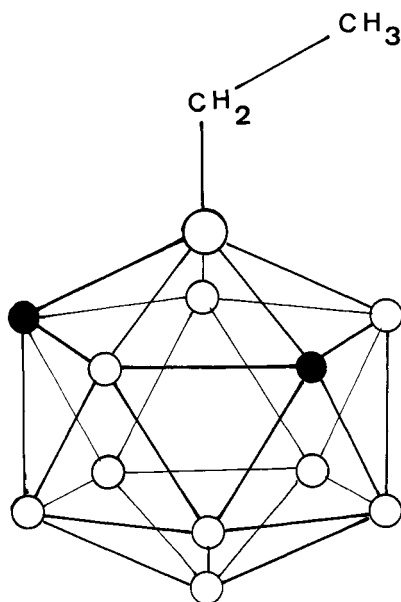


Figure 2.

5.3. Formation of Bonds

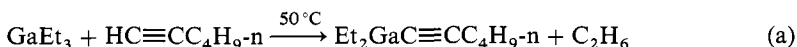
183

5.3.4. Formation of Carbon—Ga Bonds

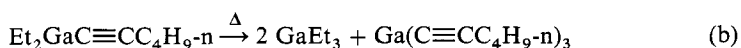
5.3.4.5. from other Organogallium Compounds or to Acetylenes

5.3.4.5. from other Organogallium Compounds or to Acetylenes**5.3.4.5.1. by Substitution of Carbon—Hydrogen for Carbon—Ga Bonds (Gallation).**

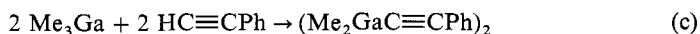
Trialkylgallanes react with terminal alkynes; e.g., GaEt₃ and 1-hexyne react¹:



This reaction should be a route to unsymmetrical alkylgallanes, but diethyldihexynylgallane disproportionates on distillation:



When GaMe₃ and phenylacetylene are heated at 50°C for 12 h in a sealed tube, dimethyl(phenylethynyl)gallane is obtained as a dimeric creamy solid:



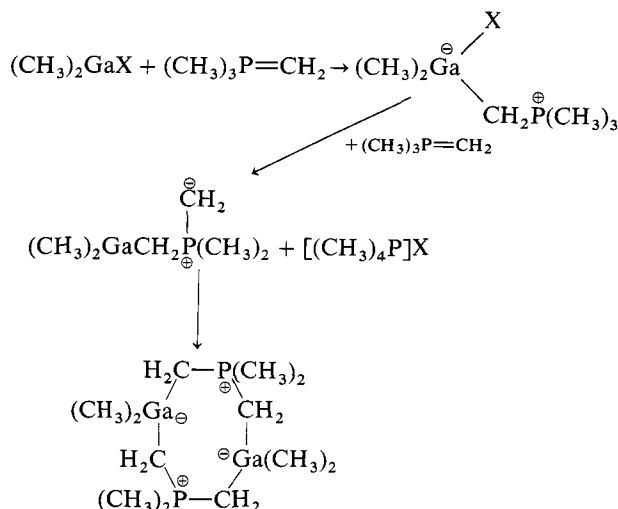
The dimer is a symmetrically bridged species with two types of Ga—C bond³, a σ bond and a strong π interaction between Ga and the π electrons of the triple bond, as shown by the length of the C≡C bond: 1.183 Å (11.83 nm) [compared to 1.204 Å (12.04 nm) in acetylene] and by the 172.8° C≡CGa angle (see Fig. 1). In tetrahydrofuran (THF) the compound redistributes:



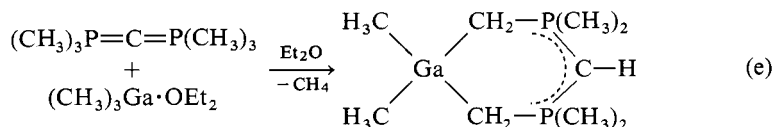
as shown by NMR.

Complexed alkynylgallanes are prepared⁴ from GaX₃ and Na[C≡CH].

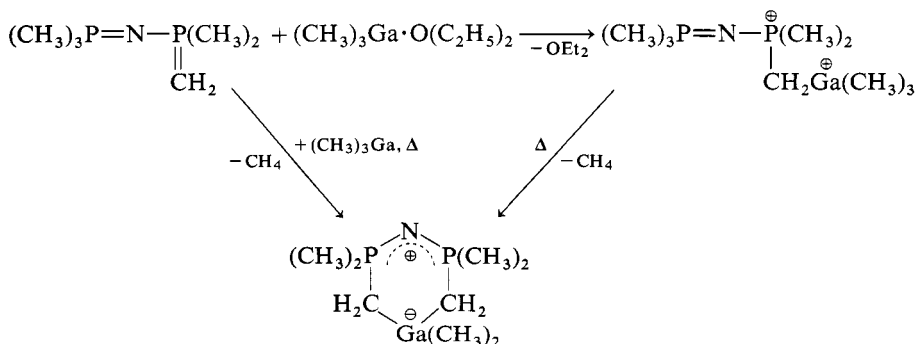
The C—H bonds vicinal to a phosphorus atom can be substituted; e.g., when Me₃P=CH₂ is reacted with 1 equiv of Me₂GaCl in benzene at 6°C during 15 h, dimeric dimethylgalladimethylphosphonium-bis(methylide) is obtained:



Cyclic dimethylgallium ylides can be obtained from hexamethylcarbodiphosphorane and $\text{Me}_3\text{Ga}\cdot\text{OEt}_2$ by direct reaction in benzene at RT. The reaction is slightly exothermic, but refluxing for 7 h in benzene is necessary⁶:



Similar compounds can be obtained from dimethyl(methylene)(trimethylphosphoranylideneamino)phosphorane⁶. Reacting this diylide in ether with a cold (0°C) solution of $\text{Me}_3\text{Ga}\cdot\text{OEt}_2$ evolves no gas, but after 2 h at RT a crystalline 1:1 adduct can be isolated from pentane. When this compound is heated and refluxed in benzene for 2 h, CH_4 is evolved and heterocyclic compounds are formed.



(J. C. MAIRE)

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2. E. A. Jeffery, T. Mole, *J. Organomet. Chem.*, **11**, 393 (1968).
3. B. Teclé, W. H. Ilsley, J. P. Oliver, *Inorg. Chem.*, **20**, 2335 (1981).
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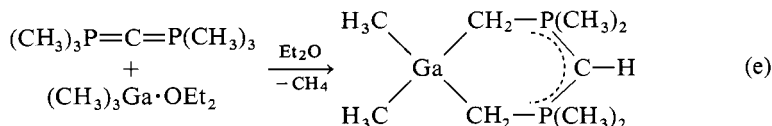
5.3.4.5.2. by Exchange of Organic Groups between Organogallanes and Other Organometallics.

This exchange metallation is seldom used, but many intra- and intermolecular examples are available. Redistribution, a special case of exchange of organic groups between two Ga atoms, occurs frequently with mixed trialkylgallanes. Diethyldecylgallium¹ redistributes at 100°C to give corresponding trialkyl derivatives. Diethylhexinylgallium¹ behaves similarly on attempted distillation at $120^\circ\text{--}150^\circ\text{C}$ at under 2 torr.

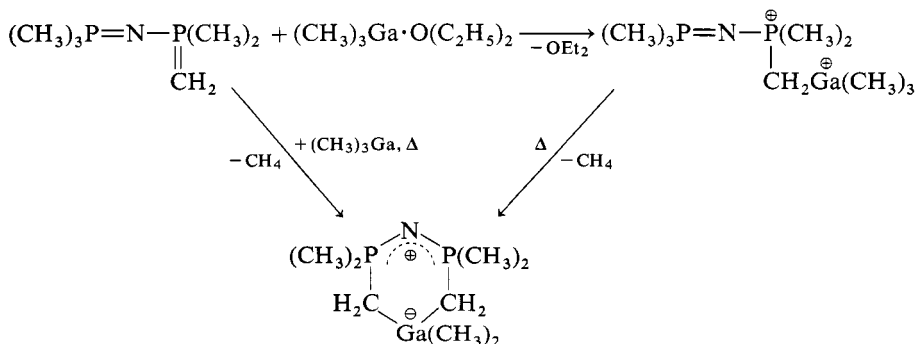
Three types of exchange can be distinguished (1) between organometallics, (2) between complexed organometallics and organometallics, and (3) between organometallic anions.

(i) Methyl-Group Exchange. Between GaMe_3 and CdMe_2 or AlMe_3 . Variable-T NMR yields energy and entropy of activation; e.g., in the $\text{GaMe}_3\text{--AlMe}_3$ system, where

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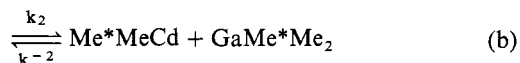
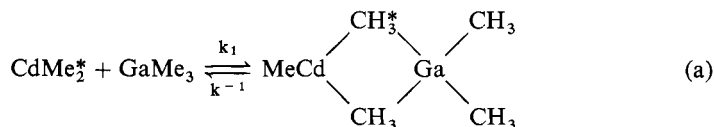
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This exchange metallation is seldom used, but many intra- and intermolecular examples are available. Redistribution, a special case of exchange of organic groups between two Ga atoms, occurs frequently with mixed trialkylgallanes. Diethyldecylgallium¹ redistributes at 100°C to give corresponding trialkyl derivatives. Diethylhexinylgallium¹ behaves similarly on attempted distillation at $120^\circ\text{--}150^\circ\text{C}$ at under 2 torr.

Three types of exchange can be distinguished (1) between organometallics, (2) between complexed organometallics and organometallics, and (3) between organometallic anions.

(i) Methyl-Group Exchange. Between GaMe_3 and CdMe_2 or AlMe_3 . Variable-T NMR yields energy and entropy of activation; e.g., in the $\text{GaMe}_3\text{--AlMe}_3$ system, where

the rate of exchange is determined by dissociation of the trimethylaluminium dimer, activation energy = 16.5 kcal mol⁻¹. The activated monomer then reacts with a molecule of GaMe₃, thereby effecting the exchange. This dissociation is typical of Al. Exchange between GaMe₃ and CdMe₂ is slower²; at -54°C in CH₂Cl₂ NMR indicates that the rate is proportional to the concentration of both species, suggesting a bimolecular mechanism involving a four-centered, bridged intermediate:



The kinetic data, assuming a steady state ($k^{-1} = k_2$), are:

$$k = 1860 \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 25^\circ\text{C}$$

$$\Delta E^\ddagger = 7.8 \pm 0.8 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -19 \text{ e.u.}$$

Solvent exerts an influence³:

	E [‡]	k	ΔS [‡]
Cyclopentane	6.7 ± 0.4	45,000	-17
Toluene	7.0 ± 0.2	1,500	-23

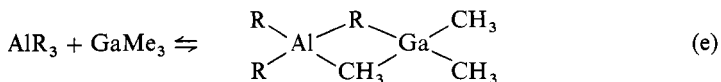
The rate depends on the coordinating nature of the solvent, the more coordinating, the slower (despite the opposite trend for the self-exchange of CdMe₂, which can be explained, assuming a four-centered intermediate, by the competition of solvent and exchanging group for the vacant orbitals of the metal).

The rate law for exchange between AlMe₃ and GaMe₃ in cyclopentane and decalin is neither a simple second-order associative nor a first-order dissociative one⁴. A cage effect is proposed for noninteracting solvents to explain why the bridge-terminal exchange in Al₂Me₆ is faster than the intermolecular exchange but this is contested.

(ii) Exchange Between Complexed Organometallics and Organometallics. If one of the organometallics is complexed by a base, a metal-carbon bond cleavage is necessary for the exchange to start, because a transition state, such as:

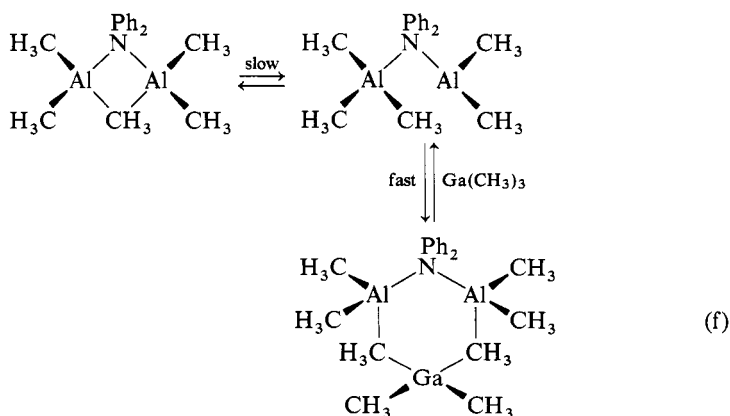


is unlikely. An alternative is:



For the reaction of GaMe_3 with $\text{AlMe}_3 \cdot \text{B}$, $\text{B} = \text{OEt}_2$, pyridine (PY) and 2,6- Me_2PY (lutidine), the rates are lutidine $>$ $\text{Et}_2\text{O} >$ PY, opposite to the order of dissociation energies of the $\text{Me}_3\text{Al} \cdot \text{B}$ compounds, and thus in agreement with initial dissociation of the adduct. In $\text{Me}_3\text{Ga} \cdot \text{NMe}_3$ – GaMe_3 , $\text{Me}_3\text{Ga} \cdot \text{PY}$ – GaMe_3 , etc., methyl groups and not only simple bases exchange, for GaMe_3 exhibits rapid exchange of methyl groups in hydrocarbons even at -100°C^5 .

Bis(μ -diphenylamino)tetramethylaluminum, (I), with GaMe_3 is first order⁶, first order in Al compound and independent of the GaMe_3 conc with activation parameters $E^\ddagger = 20.7$; $\Delta H^\ddagger = 20.1$ and $\Delta S^\ddagger = 16.0$ at 290 K. The mechanism involves as rate-determining step opening of the methyl bridge in (I). The nondependence on GaMe_3 concentration is a consequence of its high concentration relative to the activated complex.



(iii) Exchange Between Organometallic Anions. The exchange in $\text{Li}[\text{GaR}_4]$ can be detected by both ^7Li and ^1H NMR. For the $\text{LiEt} \cdot \text{LiGaEt}_4$ and $\text{LiAlEt}_4 \cdot \text{LiGaEt}_4$ systems at -60° to $+30^\circ\text{C}$ in ether⁷, the kinetics can be extracted from NMR data by measurement of half-height linewidths and by calculation of the overall lineshape for a two-site exchange as a function of the lifetime. The alkyl exchange process is slow on the NMR timescale, with the rate-determining step the formation of solvent-separated ion pairs from contact ion pairs. The Li exchange, is also rapid, with the rate-determining step the dissociation of the LiR tetramer. Both exchanges are faster with $\text{R} = \text{Et}$ than with $\text{R} = \text{Me}$.

(J. C. MAIRE)

1. J. E. Eisch, *J. Am. Chem. Soc.*, **84**, 3830 (1962).
2. K. Henold, J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 3171 (1969).
3. J. Soulati, K. Henold, J. P. Oliver, *J. Am. Chem. Soc.*, **93**, 5691 (1971).
4. T. L. Brown, L. L. Murrell, *J. Am. Chem. Soc.*, **94**, 378 (1972).
5. T. L. Brown, *Acc. Chem. Res.*, **1**, 23 (1968).
6. J. E. Rie, J. P. Oliver, *J. Organomet. Chem.*, **133**, 147 (1977).
7. K. C. Williams, T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4134 (1966).

5.3. Formation of Bonds

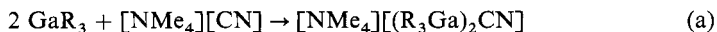
187

5.3.4. Formation of Carbon—Ga Bonds

5.3.4.5. from other Organogallium Compounds or to Acetylenes

5.3.4.5.3. by Reaction with Nitriles and Cyanide Ion.

Trimethyl- and triethylgallium react with the finely powdered, anhydr $[\text{NMe}_4][\text{CN}]$, at 85°C to give a 2:1 crystalline complex:



However, when heated at 120°C under vacuum this complex decomposes, forming 1 mol of GaR_3 and the 1:1 complex:



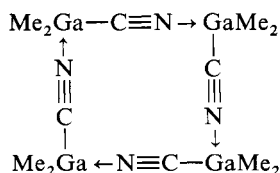
The complexes are hygroscopic and oxygen sensitive; the methyl complex is more stable than the ethyl. Vibrational spectroscopy shows that in the 1:1 complex the Ga—CN bond occurs through the carbon atom, and in the 2:1 complex, through both carbon and nitrogen atoms¹.

Similarly, when $\text{K}_2[\text{Hg}(\text{CN})_4]$ is treated with xs Me_3Ga at 95°C , ligand exchange occurs²:



Excess GaMe_3 and HgMe_2 are removed under vacuum, and the complex is isolated as a colorless, hygroscopic tetrahydrofuran- (THF) soluble compound that decomposes at 217°C . The reaction goes through the intermediates $\text{HgC}\equiv\text{N}\cdot\text{GaMe}_3$ and $(\text{Me}_2\text{GaCN})_4$, the existence of the being confirmed by its direct synthesis (see below).

Tetrameric (in benzene) Me_2GaCN can be prepared³ by reacting GaMe_3 with HCN:

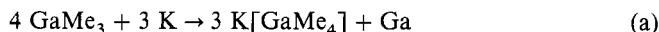


When exposed to air it deposits crystals of $(\text{Me}_2\text{GaOH})_4$. Dimethylgallium cyanide³ can be obtained by reacting GaMe_3 with Me_3GeCN in ether at RT; Me_3SnCN and Me_3PbCN can also be used.

(J. C. MAIRE)

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The $\text{Li}[\text{GaR}_4]$ ($\text{R} = \text{Me}, \text{Et}$) and the K and Rb salts ($\text{R} = \text{Me}$) are obtained from 1:2 $\text{Me}_3\text{Ga}\cdot\text{OEt}_2$ in tetrahydrofuran (THF) cooled with liq N_2 with the metal. After 1 h stirring the mixture is warmed to RT and a crystalline compound is obtained by evaporating the solvent under vacuum:



5.3. Formation of Bonds

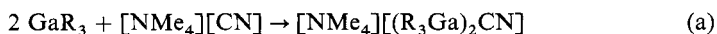
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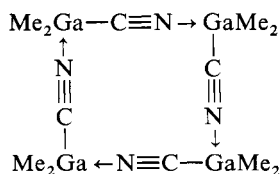
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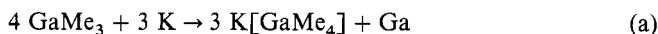


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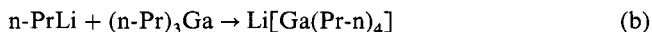
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The products are not pyrophoric¹. However, $[\text{Ga}(\text{Pr-n})_4]^-$ is obtained from² 1:1 n-PrLi and n-Pr₃Ga:



The solid product is slightly soluble in benzene, from which it can be recrystallized, it is stable at its mp. The $\text{Li}[\text{GaR}_4]$ cleaves the Sn—Sn bond in Sn_2Me_6 to give $\text{Li}[\text{Me}_3\text{SnGaR}_3]$, and $\text{Li}[\text{GaMe}_4]$ reacts with potassium metal in dimethoxyethane (glyme) to give $\text{K}_2[\text{Ga}_2\text{Me}_6]$.

Preparation of $[\text{Me}_4\text{As}][\text{GaMe}_4]$ is claimed from Me_3As and GaMe_3 ³.

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5.3.5. Formation of the Carbon—In Bond

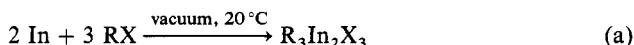
5.3.5.1. from the Elements

This topic is presented in §5.10.2.

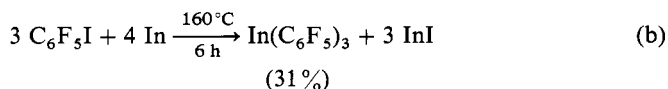
5.3.5.2. from In Metal and its Alloys

5.3.5.2.1. by the Action of Organic Halides.

The action of alkyl halides with In metal is slow and $\text{R}_3\text{In}_2\text{X}_3$ sesquihalides are formed^{1,2}:



where if $\text{X} = \text{Br}$, 3–5 days and $\text{R} = \text{Me}$, Et, n-Pr, n-Bu, and if $\text{X} = \text{I}$, the reaction takes 1–3 days and $\text{R} = \text{Me}$, Et, n-Pr, n-Bu. When $\text{C}_6\text{F}_5\text{I}$ is heated with xs In, $\text{In}(\text{C}_6\text{F}_5)_3$ can be isolated by sublimation^{3,4}:

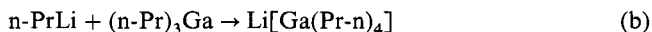


When stoichiometric amounts of $\text{C}_6\text{F}_5\text{I}$ and In are heated, $(\text{C}_6\text{F}_5)_2\text{InI}$ is obtained in addition to $\text{In}(\text{C}_6\text{F}_5)_3$. Treatment of the mixture with Et_2O followed by fractional sublimation gives, besides $(\text{C}_6\text{F}_5)_3\text{In} \cdot \text{OEt}_2$, also $\text{C}_6\text{F}_5\text{InI}_2$ and $(\text{C}_6\text{F}_5)_2\text{InI}$.

(L. RÖSCH)

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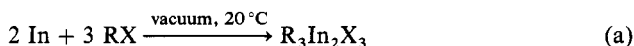
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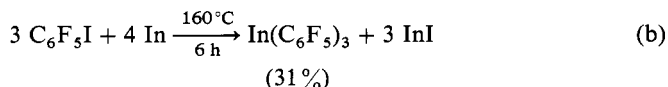
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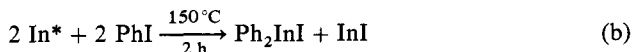
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Highly active metals can be prepared either by¹ low-T codeposition of metal vapors with solvents in xs or by² reducing a soluble metal halide with potassium or Na metal in an appropriate solvent. Both methods are used to prepare highly active In metal.

Active In, prepared by the codeposition method, with EtI gives a mixture of Et₂InI, EtInI₂ and InI. The best results are obtained with (CH₃OCH₂CH₂)₂O (diglyme) as solvent¹. Reduction of InCl₃ with potassium metal in refluxing xylene under Ar delivers highly active In (In*) metal:



By the reaction of In* with xs PhI at 150°C a nearly quantitative yield of Ph₂InI is formed³.



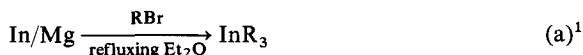
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5.3.5.2.3. by the Action of Organic Halides with In-Mg Alloy or a Mixture of In and Mg Metals.

Trialkylindanes result from In-Mg alloy or a mixture of In and Mg with alkyl-bromides in ethers^{1,2}:



where if R = Me, the yield is 87 %; if Et, 95 %; if n-Pr, 75 %; if i-Pr, 70 %; if n-Bu, 85 % and if s-Bu, 79 %. The products can be isolated by vacuum distillation. In the reaction with MeBr, a mixture of InMe₃ and InMe₃·OEt₂ is first obtained, a second distillation with added benzene gives¹ pure InMe₃.

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5.3.5.2.4. by Reaction of Cyclopentadiene with In Vapor.

When In vapor, obtained from a furnace cell, is coprecipitated with xs C₅H₆ on the cooled wall of a reaction vessel, h⁵-C₅H₅In is formed¹.

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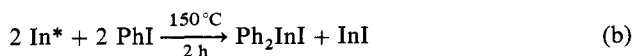
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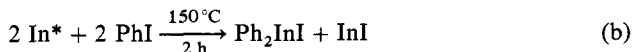
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Analogously, (MeC₆H₄)₂InI₃³, Me₂InI⁴, Et₂InI⁴ and BrIn(CH₂COOEt)₂ can be obtained in high yields.

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1. K. J. Klabunde, T. O. Murdoch, *J. Org. Chem.*, **44**, 3901 (1979).
2. R. D. Rieke, *Acc. Chem. Res.*, **10**, 301 (1977).
3. L. Chao, R. D. Rieke, *Synth. Inorg. Met.-Org. Chem.*, **5**, 165 (1975).
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5.3.5.2.3. by the Action of Organic Halides with In-Mg Alloy or a Mixture of In and Mg Metals.

Trialkylindanes result from In-Mg alloy or a mixture of In and Mg with alkyl-bromides in ethers^{1,2}:



where if R = Me, the yield is 87 %; if Et, 95 %; if n-Pr, 75 %; if i-Pr, 70 %; if n-Bu, 85 % and if s-Bu, 79 %. The products can be isolated by vacuum distillation. In the reaction with MeBr, a mixture of InMe₃ and InMe₃·OEt₂ is first obtained, a second distillation with added benzene gives¹ pure InMe₃.

(L. RÖSCH)

1. E. Todt, R. Dötzer, *Z. Anorg. Allg. Chem.*, **321**, 120 (1963).
2. E. Todt, H. Hauschildt, Ger. Pat. 1,136,702 (1962); *Chem. Abstr.*, **58**, 4597 (1963).

5.3.5.2.4. by Reaction of Cyclopentadiene with In Vapor.

When In vapor, obtained from a furnace cell, is coprecipitated with xs C₅H₆ on the cooled wall of a reaction vessel, h⁵-C₅H₅In is formed¹.

(L. RÖSCH))

1. G. M. Kuz'yants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1895 (1976).

5.3.5.2.5. by the Action of Organomercurials on In Metal.

Procedures for the preparation of organoindium compounds from In metal with organomercurials include:

1. Activated In metal with HgR_2 in toluene at ca. 50°C ¹.
2. Excess In metal at 130°C with HgR_2 , under pressure,² in the presence of a trace of I_2 .
3. Stoichiometric In metal and HgR_2 in a sealed tube at ca. 170°C ³⁻⁵.
4. Highly reactive In* metal, from reduction of InCl_3 with K or Na metal in xylene, with HgR_2 at $100^\circ\text{--}130^\circ\text{C}$. This is the quickest method with the best yields, but the yields are those estimated from the consumption of the organomercurial and not from the organoindane isolated⁶.
5. Excess In powder with HgR_2 at ca. 150°C under a positive pressure of N_2 ⁷.
6. Metallic In and HgR_2 in a sealed tube at low pressure^{8,9}.
7. Metallic In and xs HgR_2 are refluxed in toluene. This method can be used for most triaryllindanes⁷.
8. Excess In metal with HgR_2 in the presence of a trace of HgCl_2 at 100°C ¹⁰.

The triorganoindanes prepared by these methods are listed in Table 1.

TABLE 1. TRIORGANOINDANES PREPARED FROM ORGANOMERCURIALS WITH IN METAL

Organoindane	Method of preparation	Reaction time	Yield (%)	Ref.
Me_3In	2	2-3 days	75-95	2
	4	3 h	100	6
	8	8 days	^a	11
$\text{In}[(\text{CH}_2)_4\text{CH}=\text{CH}_2]_3^b$	6	^a	^a	8,9
Ph_3In	3	2 days	65-81	3
	4	2.5 h	100	6
	5	2 days	78	7
	7	60 h	78	7
$(4\text{-MeC}_6\text{H}_4)_3\text{In}$	4	2.5 h	100	6
	7	60 h	90	7
$(2\text{-MeC}_6\text{H}_4)_3\text{In}$	7	60 h	70	7
$(3\text{-MeC}_6\text{H}_4)_3\text{In}$	7	60 h	65	7
$(4\text{-EtC}_6\text{H}_4)_3\text{In}$	7	60 h	52	7
$(4\text{-Me}_3\text{CC}_6\text{H}_4)_3\text{In}$	7	60 h	87	7
$(4\text{-MeOC}_6\text{H}_4)_3\text{In}$	7	60 h	68	7
$(3\text{-FC}_6\text{H}_4)_3\text{In}$	7	60 h	71	7
$(4\text{-FC}_6\text{H}_4)_3\text{In}$	7	60 h	85	7
$(4\text{-ClC}_6\text{H}_4)_3\text{In}$	7	60 h	31	7
$(\text{C}_6\text{F}_5)_3\text{In}$	3	6 days	53	4,5
$(\text{C}_6\text{F}_5)_3\text{In}\cdot\text{Et}_2\text{O}$	3	6 days	38	4,5
$(\text{In})_3\text{In}^c$	1	^a	^a	1
$(n\text{-C}_8\text{H}_{17}\text{C}_5\text{H}_4)_3\text{In}$	1	^a	^a	1

^a Not reported.

^b Cyclization to $\text{In}[\text{CH}_2(\text{c-C}_3\text{H}_9)]_3$ occurs.

^c Ind = indenyl.

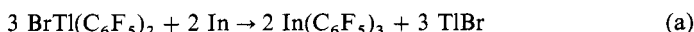
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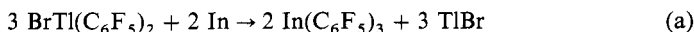
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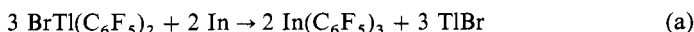
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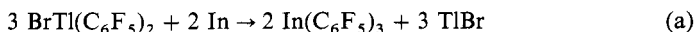
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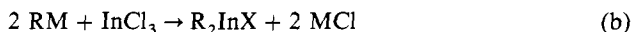
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5.3.5.3. from In Halides or Organoindium Halides

5.3.5.3.1. with More Polar Organometallics.

(i) **Organolithium and -Magnesium Reagents.** Indium(III) halides with organolithiums¹ or -magnesium halides^{2,3} leads to R_3In and diorganoindium halides, with the Mg reagents particularly favored for aryls⁴. The products can be controlled by varying the stoichiometry:



where $M = Li, MgX$; $X = \text{halide}$.

When RLi is used with $xs\ InCl_3$, the products may also vary with the time of reaction; e.g., Me_3In is obtained in good yield after the initial vigorous reaction (30 min) between 2:1 $MeLi$ and $InCl_3$. After several days, Me_2InCl is produced¹. For the sterically hindered $(Me_3Si)_2CHLi$, however, only the R_3In is produced⁵, even with $xs\ InCl_3$. Products using Li or Mg reagents are given in Table 1.

TABLE 1. COMPOUNDS FROM $In(III)$ HALIDES WITH ORGANOMAGNESIUM HALIDES OR ORGANO LITHIUMS

Compound	Method ^a	Yield (%)	Ref.
Me_3In	1a (30 min)	^b	1
Me_3In	2	50 ^c	2
Me_2InCl	1a (2-3 days)	81	1
Me_2InI	1a (2-3 days)	73	1
Et_3In	2	70	2
$n-Pr_3In$	2	70	2
$(n-Nonyl)_3In$	2	60	2
$(Me_3SiCH_2)_3In$	2	82	11
$[(Me_3Si)_2CH]_3In$	1	90	5
Ph_2InBr	2	28	2
Ph_3In	2	56 ^c	3
$(o-Tolyl)_3In$	2	54 ^c	3
$(p-Tolyl)_3In$	2	49 ^c	3
$(p-Bromophenyl)_3In$	2	43 ^c	3
$(\alpha-Naphthyl)_2InBr$	2	^b	2
$(Indenyl)_3In$	1	74 ^c	7
$(C_6F_5)_2InBr$	2	^b	12
$(C_6F_5)_2InCl$	2	^b	12
$(C_6F_5)_3In$	2	41 ^c	13
$(C_6F_5)InCl_2$	2	60 ^c	13
$(h^1-C_5H_5)_3In$	1	65	6
$(h^1-MeC_5H_4)_3In$	1	56	6

^a 1, $LiR + InCl_3$; 1a, $Lir + LiX + InCl_3$; 2, $RMgX + InCl_3$.

^b Yield not given.

^c Yield of the etherate or dioxanate.

5.3. Formation of Bonds

5.3.5. Formation of the Carbon—In Bond

5.3.5.3. from In Halides or Organoindium Halides

1. I. N. Chernykh, A. P. Tomilov, *Sov. Electrochem. (Engl. Transl.)*, 10, 971 (1974).2. J. J. Habeeb, F. F. Said, D. G. Tuck, *J. Organomet. Chem.*, 190, 325 (1980).

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TABLE 1. COMPOUNDS FROM IN(III) HALIDES WITH ORGANOMAGNESIUM HALIDES OR ORGANO LITHIUMS

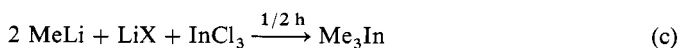
Compound	Method ^a	Yield (%)	Ref.
Me_3In	1a (30 min)	^b	1
Me_3In	2	50 ^c	2
Me_2InCl	1a (2-3 days)	81	1
Me_2InI	1a (2-3 days)	73	1
Et_3In	2	70	2
$n-Pr_3In$	2	70	2
$(n\text{-Nonyl})_3In$	2	60	2
$(Me_3SiCH_2)_3In$	2	82	11
$[(Me_3Si)_2CH]_3In$	1	90	5
Ph_2InBr	2	28	2
Ph_3In	2	56 ^c	3
$(o\text{-Tolyl})_3In$	2	54 ^c	3
$(p\text{-Tolyl})_3In$	2	49 ^c	3
$(p\text{-Bromophenyl})_3In$	2	43 ^c	3
$(\alpha\text{-Naphthyl})_2InBr$	2	^b	2
$(Indenyl)_3In$	1	74 ^c	7
$(C_6F_5)_2InBr$	2	^b	12
$(C_6F_5)_2InCl$	2	^b	12
$(C_6F_5)_3In$	2	41 ^c	13
$(C_6F_5)_3InCl_2$	2	60 ^c	13
$(h^1\text{-}C_5H_5)_3In$	1	65	6
$(h^1\text{-}MeC_5H_4)_3In$	1	56	6

^a 1, $LiR + InCl_3$; 1a, $Lir + LiX + InCl_3$; 2, $RMgX + InCl_3$.

^b Yield not given.

^c Yield of the etherate or dioxanate.

A modification of the Li reaction uses 2:1:1 MeLi, LiX and InCl₃ in Et₂O. The product isolated depends on the time of reaction¹:



where if X = Cl, the yield is 81; if X = I the yield is 73%. The formation of the dimethylindium halide is favored by the solubility order LiCl < LiI < Me₂InI. This one-step reaction is a convenient means of producing Me₂InX₂ (X = Cl, I) merely by controlling the stoichiometry and the reaction time.

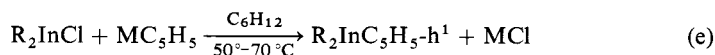
Diorganoindium halides also react with xs RLi alkylolithium to produce¹ R₃In.

Indium(I) halides also react with alkylolithiums. A suspension of InCl in Et₂O with xs LiC₅H₅ gives h⁵-C₅H₅In(I) in 72% yield¹⁴, and L₂InCl, L = 2-[(dimethylamino)methyl]phenyl, reacts with MeLi in Et₂O to produce¹⁵ L₂InMe in 77% yield after 25 h at RT.

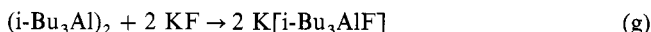
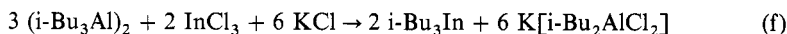
The major disadvantage of the organolithium or -magnesium reagents is the need for Et₂O or other basic solvents, which produce adducts with organoindium compounds. The solvated complex must then be decomposed to yield unsolvated products, but this is not always easy because thermal decomposition of the In compound may also occur. Isolation of In alkyls and aryls from organomagnesium reactions is improved by precipitating the compound from ether as a 1,4-dioxane complex^{2,3}. Heating under reduced pressure then typically yields free organoindium.

(ii) Organosodium and -Potassium Compounds. The greater reducing power of organosodium reagents can lead to In(I) species from In(III) starting materials; e.g., trichloroindium plus 1:4 Na[C₅H₅] in Et₂O yields⁶ h¹-C₅H₅In(I) with no (h¹-C₅H₅)₃In(III). The analogous reaction between LiC₅H₅ and InCl₃ yields In(C₅H₅-h¹)₃. Attempts to prepare In(I)indenyl or -fluorene from the corresponding Na compounds fail owing to the greater thermal stability of the In(III) compounds, which are intermediates in the reaction.

Potassium and Na cyclopentadienide are also useful for dialkylcyclopentadienyl compounds, e.g., with R₂InCl to produce R₂InC₅H₅-h¹ in 30–60% yields⁷:



(iii) Organoaluminums. Pure, ether-free triorganoindiums, even ones that are thermally unstable, are formed from R₃Al and In(III) halides in hydrocarbons^{8–10}. However, addition of various salts is critical to the separation of the product from alkylaluminum by products. For Et₃Al, KCl is required, resulting in a 67% isolated yield¹⁰ of Et₃In. For i-Bu₃Al and InCl₃, the mixture is first treated with KCl and distilled to produce a mixture of isobutylaluminum and isobutylindium. This mixture is then treated with KF, permitting the distillation of pure i-Bu₃In in 50% yield¹⁰. The potassium salts preferentially complex the volatile Al by products so that the desired R₃In can be distilled:

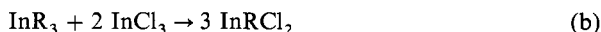
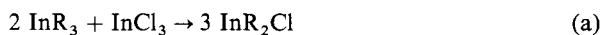


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2. F. Runge, W. Zimmerman, F. Pfeiffer, *Z. Anorg. Allg. Chem.*, **267**, 39 (1951).
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4. D. G. Tuck, in *Comprehensive Organometallic Chemistry*, Vol. 1, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 683.
5. A. J. Carty, M. J. S. Gynane, M. F. Lappert, S. J. Miles, A. Singh, N. J. Taylor, *Inorg. Chem.*, **19**, 3637 (1980).
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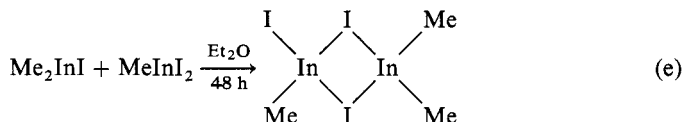
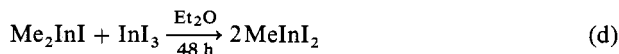
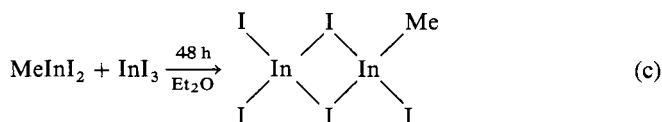
5.3.5.3.2. by Redistribution with Organoindiums.

Organoindium halides are formed nearly quantitatively by redistribution between In(III) halides and $R_3\text{In}$. Both mono- and dihalides are produced, depending on the stoichiometry:



Representative reactions are listed in Table 1.

Redistribution also takes place between In(III) halides and organoindium halides or between different organoindium halides. Methylindium iodides are produced in this manner¹:



Similarly, $(\text{h}^1\text{-C}_3\text{H}_5)_2\text{InI}$ is formed² from the redistribution of $\text{h}^1\text{-C}_5\text{H}_5\text{InI}_2$ and $(\text{h}^1\text{-C}_5\text{H}_5)_3\text{In}$.

5.3. Formation of Bonds

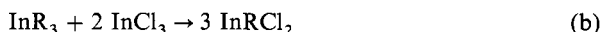
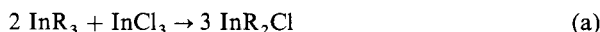
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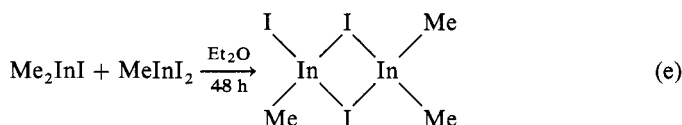
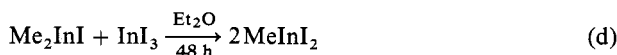
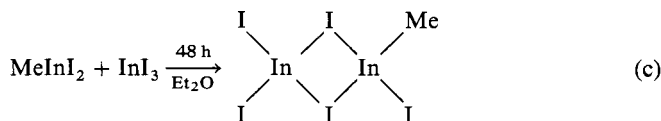
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TABLE 1. REDISTRIBUTIONS OF InR_3 AND InX_3

R	X	Ratio of $\text{InR}_3:\text{InX}_3$	Solvent	Time	Product	Yield	Ref.
Me	Cl	1:2	pentane		InRCl_2	^a	3
Et	Cl	2:1	pentane	30 min	InR_2Cl	82%	4
CH_2SiMe_3	Cl	2:1	benzene or ether	9 h	InR_2Cl	quant.	5
CH_2SiMe_3	Cl	1:2	ether	19 h	InRCl_2	quant.	5
C_6H_5	Br	2:1	benzene	8 h	InR_2Br	^a	6

^a No yield given.

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5.3.5.3.3. by the Oxidative Insertion of In(I) Halide into an Alkyl-Halide Bond.

Alkylindium diiodides or dibromides can be prepared in high yield by the insertion of the In(I) halide into the C—X bond of alkyl halides:



where R = Me, Et, n-Pr, n-Bu; X = I, Br. The reactions (I and Br), however, differ considerably.

Reactions between InI and xs RI are complete in 24 h at RT, producing nearly quantitative yields of the organoindium dihalide^{1,2}. Reactions between RBr and InBr are much slower. For MeBr and EtBr, ca. 1 week at RT is required and n-PrBr and n-BuBr require 3–4 weeks¹. The rates of the bromide reactions are increased by heating to 50°C. Reactions then reach completion in 3 days, with little or no decrease in the yield¹.

With no solvent, the more reactive halides, such as allyl or benzyl (I or Br), produce colored products that are presumably hydrocarbon polymers². However, if the reaction is run in dioxane, the organoindium dihalides can be isolated³ as the 1,4-dioxanates in approximately ca.12 h.

Indium dibromide and MeBr undergo a similar oxidative addition to form MeInBr_2 and InBr_3 . However, the products are difficult to separate, making the method of little practical synthetic value.⁴

The normally insoluble In(I) halides are soluble in aromatics or CH_2Cl_2 containing neutral organic bases⁵. These solutions are stable below ca. –20°C, but react with substrates at ca. RT. The reaction between EtBr and InBr in CH_2Cl_2 and N,N,N',N'-tetramethylethanediamine (TMED) proceeds smoothly to give $\text{EtBr}_2\text{In} \cdot \text{TMED}$ in quantitative yield.

The reaction of InCl_3 with InX (X = Cl, Br, I) in CH_2Cl_2 /toluene/TMED yields bis(TMED) adducts of $\text{Cl(X)InCH}_2\text{InCl}_2$ ⁶.

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5.3. Formation of Bonds

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5.3.5. Formation of the Carbon—In Bond

5.3.5.3. from In Halides or Organoindium Halides

TABLE 1. REDISTRIBUTIONS OF InR_3 AND InX_3

R	X	Ratio of $\text{InR}_3:\text{InX}_3$	Solvent	Time	Product	Yield	Ref.
Me	Cl	1:2	pentane		InRCl_2	^a	3
Et	Cl	2:1	pentane	30 min	InR_2Cl	82%	4
CH_2SiMe_3	Cl	2:1	benzene or ether	9 h	InR_2Cl	quant.	5
CH_2SiMe_3	Cl	1:2	ether	19 h	InRCl_2	quant.	5
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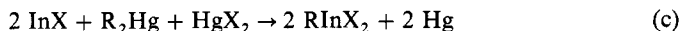
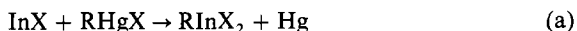
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5.3.5.3.4. by Oxidative Arylation of In(I) Halides by Arylmercurials.

Although In(I) halides do not insert directly into aryl-halide bonds, oxidative arylation does occur with In(I) halides and arylmercurials in good yield¹. The arylmercurial may be an arylmercurial halide or the bis(aryl)mercurial:



where X = Cl, Br, I; R = C₆H₅, p-F-C₆H₄, p-tolyl. Qualitatively, the rate of formation is in the order Cl > Br > I. The rate of formation of the arylindium dihalides (Table 1) is faster than that of the diarylindium halides.

TABLE 1. ARYLINDIUMS FROM OXIDATIVE ARYLATION OF ARYLMERCURIALS¹

Compound	Reaction	Yield (%)
PhInCl ₂	a,c	81-90
PhInBr ₂	a,c	71-96
PhInI ₂	c	88
Ph ₂ InCl	b	64-66
Ph ₂ InBr	b	77-84
Ph ₂ InI	b	92
(4-F-Ph) ₂ InBr	b	73
(4-F-Ph)InBr ₂	c	82
(p-tolyl) ₂ InBr	b	95
(p-tolyl)InBr ₂	c	94

^a InX + RHgX.

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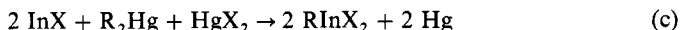
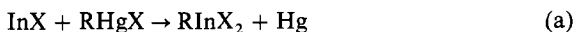
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Although In(I) halides do not insert directly into aryl-halide bonds, oxidative arylation does occur with In(I) halides and arylmercurials in good yield¹. The arylmercurial may be an arylmercurial halide or the bis(aryl)mercurial:



where X = Cl, Br, I; R = C₆H₅, p-F-C₆H₄, p-tolyl. Qualitatively, the rate of formation is in the order Cl > Br > I. The rate of formation of the arylindium dihalides (Table 1) is faster than that of the diarylindium halides.

TABLE 1. ARYLINDIUMS FROM OXIDATIVE ARYLATION OF ARYLMERCURIALS¹

Compound	Reaction	Yield (%)
PhInCl ₂	a,c	81-90
PhInBr ₂	a,c	71-96
PhInI ₂	c	88
Ph ₂ InCl	b	64-66
Ph ₂ InBr	b	77-84
Ph ₂ InI	b	92
(4-F-Ph) ₂ InBr	b	73
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(p-tolyl) ₂ InBr	b	95
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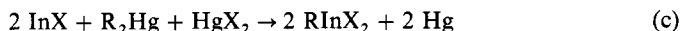
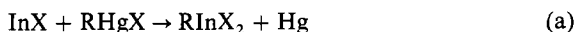
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5.3. Formation of Bonds

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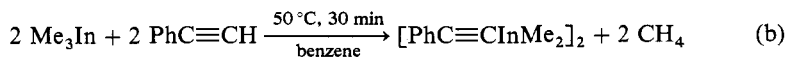
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5.3.5.4.2. by Substitution of Acidic Carbon—Hydrogen bonds by Carbon—In Bonds (Irradiation).

The absence of suitable hydrogen atoms attached to carbon normally prevents the synthesis of R_2MR' molecules by alkane elimination. However, several examples are known. Trimethylindium or $[Me_2InNMe_2]_2$, formed from Me_3In and $HNMe_2$ reacts with freshly distilled cyclopentadiene at RT in hydrocarbon solvent to precipitate $Me_2InC_5H_5-h^1$ after 48 h in > 70% yield¹:



Trimethylindium also reacts² with $PhC\equiv CH$:



Trimethylindium reacts with $Me_3P=CH_2$ to form the stable, but highly reactive, adduct³ $Me_3PCH_2InMe_3$. Reaction of 2:1 $Me_3P=CH_2$ with Me_2InX ($X = Cl, Br$), on the other hand, produces a cyclic ylide⁴, $(InMe_2CH_2PMe_2CH_2)_2$.

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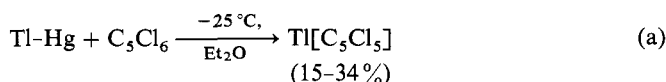
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Reaction of Tl metal with organic halides is not favored, and only rarely is it possible to get organothalliums this way.

Prolonged shaking of Na-Tl alloys with $EtCl$ at RT gives $TlEt_3$ in low yield¹. With MeI no reaction occurs with massive Tl metal or Na-Tl alloy².

Unstable $Tl [C_5Cl_5]$ is obtained³ from Tl-Hg and C_5Cl_6 :



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5.3. Formation of Bonds

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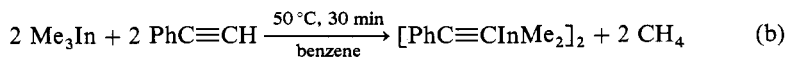
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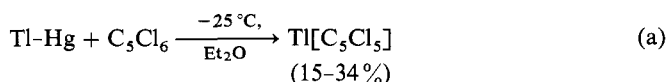
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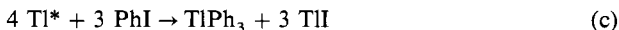


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When Tl vapor, obtained from a high-T cell, is coprecipitated with xs C_5H_6 on the cooled wall of a reaction vessel, $\text{TlC}_5\text{H}_5\text{-h}^5$ is formed¹.

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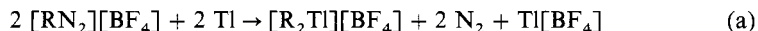
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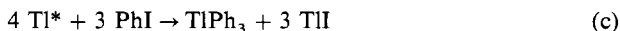
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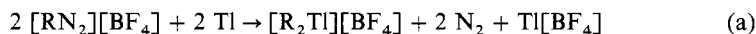
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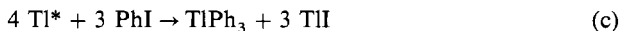
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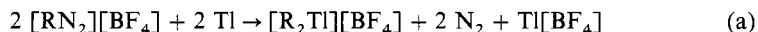
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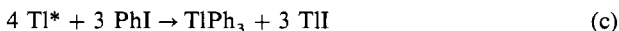
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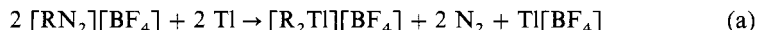
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1. A. N. Nesmeyanov, K. A. Kocheshkov, eds., *Methods of Elemento-Organic Chemistry*, Vol. 1, North Holland, Amsterdam, 1967, p. 579.

5.3.6.2.5. by the Decomposition of Aryldiazonium Fluoroborates.

Aromatic R_2TlCl compounds can be prepared in moderate yields from $[\text{RN}_2][\text{BF}_4]$ and Tl metal or Na-Tl alloy:



where $\text{R} = \text{Ph}$, $2\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$, $4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4$, $4\text{-C}_2\text{H}_5\text{OOC}_6\text{H}_4$. The products compounds can be isolated as the diarylthallium chlorides. The yield of Ph_2TlCl is 10–20%; the other yields are $\leq 10\%^1$.

(L. RÖSCH)

5.3. Formation of Bonds

5.3.6. Formation of Carbon—Tl Bonds

5.3.6.2. from Tl Metal and its Alloys

Reduction of TlCl with K metal in xylene yields a finely divided black powder of Tl of exceptional reactivity:



This Tl^* powder reacts with PhI and TlPh_3 is obtained⁴:



(L. RÖSCH)

1. A. N. Nesmeyanov, K. A. Kocheshkov, eds., *Methods of Elemento-Organic Chemistry*, Vol. 1, North Holland, Amsterdam, 1967, p. 551.
2. A. G. Lee, *The Chemistry of Thallium*, Elsevier, Amsterdam, 1971.
3. G. Wulfsberg, R. West, *J. Am. Chem. Soc.*, **94**, 6069 (1972).
4. R. D. Rieke, *Acc. Chem. Res.*, **10**, 301 (1977).

5.3.6.2.2. by Reaction of Cyclopentadiene with Tl Vapor.

When Tl vapor, obtained from a high-T cell, is coprecipitated with xs C_5H_6 on the cooled wall of a reaction vessel, $\text{TlC}_5\text{H}_5\text{-h}^5$ is formed¹.

(L. RÖSCH)

1. G. M. Kuz'yants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1895 (1976).

5.3.6.2.3. by Pyrolysis of Hydrocarbons.

The pyrolysis of several hydrocarbons, such as $\text{c-C}_7\text{H}_{12}$ or $\text{c-C}_6\text{H}_{10}$, in the presence of Tl metal gives $\text{TlC}_5\text{H}_5\text{-h}^5$ in low yields¹.

(L. RÖSCH)

1. J. M. Lalancette, A. Lachance, *Can. J. Chem.*, **49**, 2996 (1971).

5.3.6.2.4. by the Action of Diarylthallonium Fluoroborates.

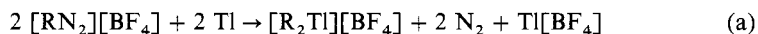
Metallic Tl reacts with $(\text{Ph}_2\text{X})\text{BF}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) at RT in acetone with formation of $[\text{Ph}_2\text{Tl}][\text{BF}_4]$ in modest yields¹.

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1. A. N. Nesmeyanov, K. A. Kocheshkov, eds., *Methods of Elemento-Organic Chemistry*, Vol. 1, North Holland, Amsterdam, 1967, p. 579.

5.3.6.2.5. by the Decomposition of Aryldiazonium Fluoroborates.

Aromatic R_2TlCl compounds can be prepared in moderate yields from $[\text{RN}_2][\text{BF}_4]$ and Tl metal or Na-Tl alloy:



where $\text{R} = \text{Ph}$, $2\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$, $4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4$, $4\text{-C}_2\text{H}_5\text{OOC}_6\text{H}_4$. The products compounds can be isolated as the diarylthallium chlorides. The yield of Ph_2TlCl is 10–20%; the other yields are $\leq 10\%^1$.

(L. RÖSCH)

1. A. N. Nesmeyanov, K. A. Kocheshkov, eds., *Methods of Elemento-Organic Chemistry*, Vol. 1, North Holland, Amsterdam, 1967, p. 579.

5.3.6.2.6. by Action of Organomercurials.

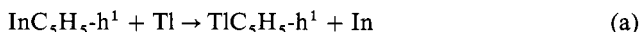
Activated Tl metal reacts with $\text{Hg}(\text{C}_5\text{H}_5\text{-h}^1)_2$ in hydrocarbon or ethers to give $\text{TlC}_5\text{H}_5\text{-h}^1$ in high yield¹.

(L. RÖSCH)

1. J. R. Mangham, US Pat. 2,969,382 (1961); *Chem. Abstr.*, 55, 11,332 (1961).

5.3.6.2.7. by Action of $\text{InC}_5\text{H}_5\text{-h}^1$.

The reaction:



is performed by mixing $\text{InC}_5\text{H}_5\text{-h}^1$ with finely divided Tl metal, followed by heating the mixture under high vacuum. The $\text{TlC}_5\text{H}_5\text{-h}^1$, formed by exchange, sublimes¹.

(L. RÖSCH)

1. J. M. Lalancette, A. Lachance, *Can. J. Chem.*, 49, 2996 (1971).

5.3.6.2.8. by Electrolysis of Organoalanes at a Tl Anode.

Electrolysis of R_3Al in a conducting medium using an anode of the 2nd to 5th periodic groups delivers the alkylmetal compounds^{1,2}.

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1. K. Ziegler, Br. Pat. 814,609 (1959); *Chem. Abstr.*, 53, 17,733 (1959).
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5.3.6.2.9. by Electrolysis of Organic Halides at a Tl Cathode.

Diorganothallium iodides R_2TlI ($\text{R} = \text{CH}_2\text{CH}_2\text{CN}$, Me, Et) can be prepared by electrolyzing $\text{ICH}_2\text{CH}_2\text{CN}$, MeI or EtI in aq K_2HPO_4 using a Tl cathode and a Pt-wire anode separated by a ceramic diaphragm^{1,2}.

(L. RÖSCH)

1. I. N. Chernykh, A. P. Tomilov, *Sov. Electrochem. (Engl. Transl.)*, 10, 971 (1974).
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5.3.6.3. from Tl(I) or Tl(III) Salts or Organothallium (III) Halides

5.3.6.3.1. with More Active Organometallics.

Organometallics react with Tl halides to produce C—Tl bonds. The actual Tl compound isolated depends on the organometallic, the Tl halide and the conditions^{1–5}.

5.3. Formation of Bonds

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5.3.6. Formation of Carbon—Tl Bonds

5.3.6.3. from Tl(I) or Tl(III) Salts

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5.3.6.2.6. by Action of Organomercurials.

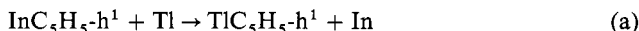
Activated Tl metal reacts with $\text{Hg}(\text{C}_5\text{H}_5\text{-h}^1)_2$ in hydrocarbon or ethers to give $\text{TlC}_5\text{H}_5\text{-h}^1$ in high yield¹.

(L. RÖSCH)

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5.3.6.2.7. by Action of $\text{InC}_5\text{H}_5\text{-h}^1$.

The reaction:



is performed by mixing $\text{InC}_5\text{H}_5\text{-h}^1$ with finely divided Tl metal, followed by heating the mixture under high vacuum. The $\text{TlC}_5\text{H}_5\text{-h}^1$, formed by exchange, sublimes¹.

(L. RÖSCH)

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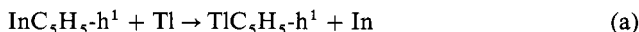
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The reaction:



is performed by mixing $\text{InC}_5\text{H}_5\text{-h}^1$ with finely divided Tl metal, followed by heating the mixture under high vacuum. The $\text{TlC}_5\text{H}_5\text{-h}^1$, formed by exchange, sublimes¹.

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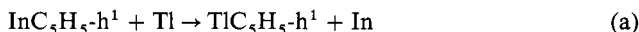
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The reaction:



is performed by mixing $\text{InC}_5\text{H}_5\text{-h}^1$ with finely divided Tl metal, followed by heating the mixture under high vacuum. The $\text{TlC}_5\text{H}_5\text{-h}^1$, formed by exchange, sublimes¹.

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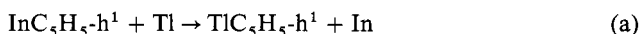
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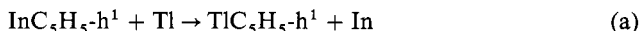
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The reaction:



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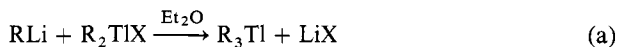
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5.3.6.3.1. with More Active Organometallics.

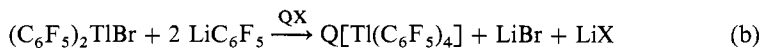
Organometallics react with Tl halides to produce C—Tl bonds. The actual Tl compound isolated depends on the organometallic, the Tl halide and the conditions^{1–5}.

Organolithiums react with diorganothallium halides in ether to produce R_3Tl :



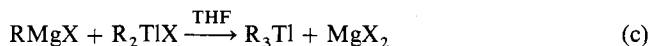
This is the most common and widely applicable route⁶⁻⁸ to R_3Tl . If the organothallium halide and the organolithium contain different organo groups, it is also a means of producing mixed R_2TlR' .

Solid $[R_4Tl]$ salts precipitate⁹ from xs RLi with diorganothallium halides in the presence of bulky cations:



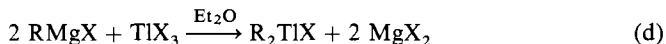
where $X = Cl, Br$; $Q = [Et_4N], [n-Bu_4N], [Ph_3BzP]$.

Organomagnesium halide with R_2TlX halide:



is not successful unless the organic group is electronegative, such as penta(fluoro)phenyl¹⁰, or the reaction is run in a strongly coordinating solvent, such as tetrahydrofuran (THF)¹¹.

Excess organomagnesium halide does react with Tl(III) halides or carboxylates in ether to produce diorganothallium(III) compounds:



Owing to oxidation of the organomagnesium halide by Tl(III), yields are only moderate, especially for iodides and for secondary alkyls⁴. As with the diorganothallium(III) halides, thallium(III) halides with organomagnesium halides do not lead to complete substitution of halide unless coordinating solvents, such as THF, are used. Organolithiums react with Tl(III) halides in an analogous manner to produce diorganothallium(III) halides¹²⁻¹⁷.

One of the disadvantages of organolithiums or organomagnesium halides with Tl(III) halides is the need for anhydrous conditions. Both Tl(III) chloride and bromide are hygroscopic and unstable at $>RT$. Hydrated $TlCl_3$, produced by treating an aq suspension of Tl(I) halide with halogen and sweeping out xs halogen with N_2 , is dissolved in abs ether and then treated with a suitable drying agent, such as¹⁸ anhydr $CuSO_4$.

Organomagnesium halides ($R =$ straight-chain alkyls of 1-10 carbons) react with $TlBr$ to produce diorganothallium halides in moderate yields¹⁹:



where $R = n$ -alkyl. However, for secondary alkyl or aromatic groups without ortho substitution, only the coupled dialkyls or diaryls are produced²⁰.

Although no longer used preparatively, Tl(III) halides also react with organozincs²¹ and with selected organoaluminums²² to produce diorganothallium halides.

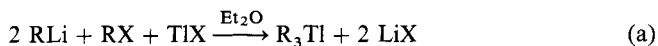
(R. D. THOMAS)

1. H. Kurosawa, in *Comprehensive Organometallic Chemistry*, Vol. 1, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 725.
2. A. G. Lee, in *Organometallic Reactions*, Vol. 5, E. I. Becker, M. Tsutsui, eds. Wiley, New York, 1975, p. 1.
3. H. Kurosawa, R. Okawara, *Organomet. Chem. Rev. (A)*, 6, 65 (1970).
4. A. G. Lee, *Q. Rev. Chem. Soc.*, 24, 310 (1970).

5. A. N. Nesmeyanov, K. A. Kocheshkov, in *Methods of Elemento-Organic Chemistry*, Vol. 1, *The Organic Compounds of Boron, Aluminum, Gallium, Indium and Thallium*, North-Holland, Amsterdam, 1967.
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5.3.6.3.2. by Action of Tl(I) Halide with an Active Organometallic and an Organic Halide.

A convenient one-step method of preparing R_3In in high yields is the reaction between Tl(I) halide and organolithiums in the presence of the corresponding organic halides:



Although most often used¹ for Me_3Tl , for which it is the preferred synthesis, Et_3Tl ², Ph_3Tl ² and $(h^5-C_5H_5FeC_5H_4)_3Tl$ ³ are also produced.

Dry Tl(I) halide and a small xs of organolithium react at RT in ether, followed by addition of xs organic halide. Both TlCl and TlI are used with comparable results, but RI significantly improves the yield² of the R_3Tl . Examples are shown in Table 1.

TABLE 1. COMPOUNDS FROM Tl(I) HALIDE AND ORGANOLITHIUMS IN THE PRESENCE OF ORGANIC HALIDE

R	TlX	RX	Yield of TlR_3 (%)	Ref.
Me	TlI	MeI	100 ^a	1
Et	TlCl	EtI	100 ^b	2
Et	TlCl	EtBr	91 ^b	2
Et	TlCl	EtCl	79 ^b	2
Ph	TlCl	PhI	79 ^b	2
Ferrocenyl	TlCl	FcI	30	3

^a In 90% yield after 1 h, quantitative if allowed to stand for 36 h.

^b Yield is based on amount of R_2TlX produced on treatment of mixture with HX.

5.3. Formation of Bonds

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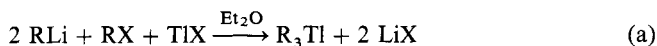
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5.3.6.3. from Tl(I) or Tl(III) Salts

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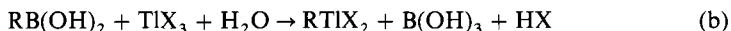
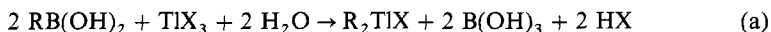
The R_3Tl do not make stable etherates and can be isolated by distillation. The Ph_3Tl may be recrystallized.

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5.3.6.3.3. with an Organoboronic Acid.

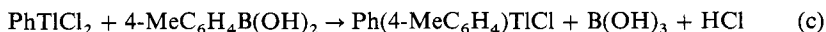
Because $TlCl_3$ and $TlBr_3$ are hygroscopic and unstable at $>RT$, their preparation and use in H_2O are highly advantageous. Both diaryl and monoaryl Tl derivatives can be prepared conveniently in H_2O by the corresponding organoboronic acids with TlX_3 ($X = \text{halogen, carboxylate}$). The stoichiometry can be used to control the products:



where $R = \text{aryl, vinyl}$; $X = Cl, Br, \text{carboxylate}$.

The monoaryllithallium halides are obtained by boiling the corresponding arylboronic acid with xs $Tl(III)$ halide in H_2O for 20–30 min. The diaryllithallium halides are produced by boiling equimolar $Tl(III)$ halide and arylboronic acid for 5–6 h. The mono- and dichlorides can be separated owing to their differing solubility in H_2O . The dibromide is also readily separable, but the monobromide decomposes to Ar_2TlBr and $TlBr_3$. Substituted phenyls are synthesized in this manner^{1–6}, with yields of 30–85%.

Organoboronic acids also react with arylthallium(III) dihalides. This is a route to mixed diorganothalliums²:



Vinylboronic acids undergo analogous reactions to give the mono- and divinylthallium derivatives in high yields^{7–9} with retention of configuration, e.g., heating a 1:1 cis-propenylboronic acid and $Tl(III)$ chloride in aq ether for 8.5 h produces 30% cis-propenylthallium dichloride and 30% bis(cis-propenyl)thallium chloride. The same reaction with trans-propenylboronic acid produces 28% trans-propenylthallium dichloride and 67% bis(trans-propenyl)thallium chloride.

Similar reactions of $Tl(III)$ halides with alkylboronic acids give only a small amount of dialkylthallium halide. The main product^{2,10} is $TlCl$.

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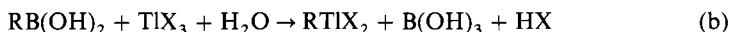
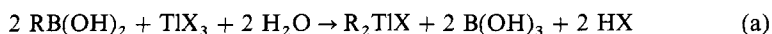
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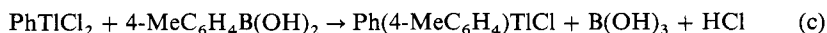
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5.3. Formation of Bonds

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5.3.6. Formation of Carbon—Tl Bonds

5.3.6.3. from Tl(I) or Tl(III) Salts

5.3.6.3.4. by Substitution of Acidic C—H Bonds by C—Tl Bonds (Thallation).

(i) Tl(III) Salts. Direct formation of carbon—Tl bonds is possible by substitution of acidic carbon—hydrogen bonds by carbon—Tl bonds. Thallium(III) carboxylates and aromatic hydrocarbons under mild conditions undergo aromatic electrophilic substitution to produce arylthallium bis(carboxylates):



where $\text{R} = \text{CH}_3, \text{CF}_3, \text{CH}(\text{CH}_3)_2$. The ease of the reaction depends on the Tl salt and the aromatic hydrocarbon. Substitution patterns can be controlled by selection of conditions^{1,2}.

Thallium(III) isobutyrate³, a weak electrophile, limits the range of aromatic substrates that can be thallated. Even for activated substrates, 100–110°C is required.

A more powerful and versatile thallating agent is Tl(III) trifluoroacetate^{4,5}. Reaction of Tl(III) trifluoroacetate with substrates activated toward electrophilic substitution is complete within a few minutes at RT. Thallation of deactivated substrates, such as halobenzenes, requires longer times at RT (48 h) or 30 min at reflux (73°C for trifluoroacetic acid). Deactivated compounds such as benzoic acid or α, α, α -trifluorotoluene are thallated after 21 and 98 h, respectively.

Under conditions of kinetic control (low T and short times), the orientation of aromatic thallation relative to substituents on the ring may generally be predicted by normal meta- vs. ortho-para-directing character of the substituents^{1,2}. For ortho-para directors, para substitution predominates owing to the steric requirements of the Tl reagent.

However, because the reaction is reversible, different products can be produced when it is run under conditions of thermodynamic control (longer times and higher T, typically 73°C, the reflux T of trifluoroacetic acid). For these cases the meta isomer may accumulate at the expense of the kinetically favored ortho and para isomers. For example, p-tolylthallium bis(trifluoroacetate) rearranges to ca. 30% of the meta isomer when heated in trifluoroacetic acid⁶.

However, the meta isomer is not necessarily the thermodynamically favored product. For substituents with which intramolecular $\text{O} \rightarrow \text{Tl}$ coordination can take place, the ortho isomer is typically the most thermodynamically stable; e.g., 1:1 Tl(III) trifluoroacetate and methylphenyl or ethylphenyl ether after short times (< 1 h) produces the kinetically favored para-thallated products. However, after long times (> 50 h) the thermodynamically more stable ortho-thallated products are produced⁷. Even under kinetic conditions, compounds with basic substituents that can form a five- or six-membered ring chelated to the ortho position lead to predominant or exclusive ortho substitution; e.g., benzoic acid undergoes ortho substitution⁴.

Excess Tl(III) trifluoroacetate can lead to dithallation, despite the deactivating character of the Tl substituent⁷. Thiophene undergoes quantitative dithallation, whereas toluene, benzene, and meta-xylene undergo partial dithallation (see Table 1).

Thallium(III) trifluoroacetate is prepared in >90% yield by heating a suspension of Tl(III) oxide in trifluoroacetic acid. This mixture can be used directly for thallation. Oxidative coupling of electron-rich arenes may be avoided by using 1:1 Tl(III) trifluoroacetate and ether in trifluoroacetic acid⁸. For acid-sensitive substrates, it is preferable first to isolate the solid Tl(III) trifluoroacetate by evaporation of the acid. This can then be used in CH_3CN as the thallating agent⁴.

5.3. Formation of Bonds
 5.3.6. Formation of Carbon—Ti Bonds
 5.3.6.3. from Ti(I) or Ti(III) Salts

TABLE 1. YIELD OF THALLATION OF AROMATIC HYDROCARBONS

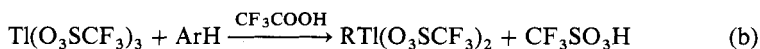
Thallated compound	Thallating agent ^a	Time	T (°C)	Yield ^b (%)	Substitution
Benzene	A	18 h	100	90	
Benzene	B			48 (96°)	
Benzene	C	75 h	73	47°	monosubstituted
				14°	meta disubstituted
Benzene	C	72 h	81	15°	monosubstituted
				1°	meta disubstituted
Benzene	C	168 h	25	28°	
Toluene	A	1 h	110	55	mixture
Toluene	B			75 (75°)	para
Toluene	C	168 h	25	92°	o, 11 %; m, 0 %;
					p, 88 %
Toluene	C	22 h	73	57°	o, 13 %; m, 19 %;
					p, 14 %; di, 14 %
Napthalene	A	1 h	115	25	2-position
Anisole	A	30–40 min	100	44	para
Phenetole	A	1 h	100	25	para
o-Dimethoxybenzene	A	45 min	100	75	4-position
m-Dimethoxybenzene	A	45 min	100	73	
p-Dimethoxybenzene	A	105 min	100	54	
1,3,5-Trimethoxybenzene	A	30 min	100	87	
Fluorobenzene	B			30 (70°)	para
Chlorobenzene	B			85 (80°)	
m-Dimethylbenzene	B			78 (100°)	6-position
p-Dimethylbenzene	B			80 (91°)	
1,3,5-Trimethylbenzene	B			34 (94°)	
Thiophene	A	5 min	100	88	2-position
Thiophene	C	6 days	25	100°	2,5-disubstitution
Acetophenone	A	5 min	100	45	2,2-disubstitution
Dibenzofuran	A	2 h	110	50	2-position
Dibenzofuran	E	4 h	165	9	4-position
Benzoic acid	B			79 (76°)	ortho
1,2,4,5-Tetrafluorobenzene	B	192 h		4	
1,2,4,5-Tetrafluorobenzene	D	20 h		39	

^a A, $\text{Ti}[\text{O}_2\text{CCH}(\text{CH}_3)_2]_3$, ref. 3; B, $\text{Ti}(\text{O}_2\text{CCF}_3)_3$, ref. 4; C, xs $\text{Ti}(\text{O}_2\text{CCF}_3)_3$, ref. 7; D, $\text{Ti}(\text{O}_3\text{SCF}_3)_3$, ref. 9; E, TiCl_3 , ref. 10.

^b Yield of isolated ArTiX_2 .

^c Yield of iodoarenes after treatment of the product mixture with iodide ions.

Thallation of species deactivated to electrophilic substitution requires more vigorous conditions, but Tl(III) trifluoroacetate decomposes above 100°C. The thallating ability of Tl(III) trifluoroacetate can be improved by the addition of electron-pair acceptor acids, such as ⁹ BF₃ or SbF₅. Another approach is the use of the even more powerful thallating agent, Tl(III) trifluoromethanesulfonate, formed from Tl(III) oxide and trifluoromethane sulfonic acid. It reacts with even unreactive polyfluoroarenes to produce arylthallium bis(trifluoromethanesulfonate)¹⁰:

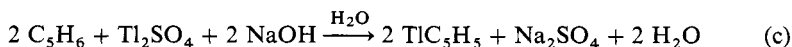


where R = p-C₆F₄OMe, p-C₆F₄Me, m-C₆F₄H, p-C₆F₄H, o-C₆F₄H, C₆F₅, 3,5-C₆F₃H₂, 3,6-C₆F₃H₂. For example, thallation of 1,2,4,5-tetrafluorobenzene by Tl(III) trifluoroacetate results in only 4% yield after 192 h. On the other hand, thallation of the same compound by Tl(III) trifluoromethanesulfonate gives a 39% yield in only 20 h. Thallium(III) trifluoroacetate in fluorosulfuric acid with SbF₅ is an even more powerful thallating agent¹¹.

Not all the polyfluorophenylthallium compounds are isolated. Attempts to recrystallize the products lead to at least partial rearrangement to bis(polyfluorophenyl)thallium(III) species.

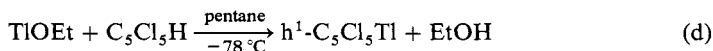
Thallation is carried out using other Tl(III) salts, including chloride¹², nitrate¹³, trichloroacetate¹⁴ and perchlorate¹⁵, but these are less important synthetically.

(ii) Tl(I) Salts. Although the reaction is not referred to as thallation, the acidic C—H bond in cyclopentadiene reacts with Tl(I) salts to produce cyclopentadienylthallium¹⁶:



Freshly distilled cyclopentadiene is added dropwise to aq NaOH and Tl(I) sulfate. The insoluble product is then filtered and sublimed. Deuterated cyclopentadienylthallium can be prepared¹⁷ in a D₂O solution of NaOD. Although the rate of deuterium-hydrogen exchange depends on the NaOD concentration, in 3.5 h product can be collected quantitatively that is 90% TlC₅D₅ and 10% TlC₅D₄H.

Ring-substituted analogues can be made similarly^{18,19}, although reduced stability to H₂O, O₂ and heat may require anhydr conditions and low T for some compounds²⁰:



(R. D. THOMAS)

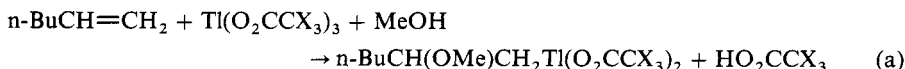
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6. H. C. Bell, J. R. Kalman, J. T. Pinhey, S. Sternhell, *Tetrahedron Lett.*, 3391 (1974).
7. G. B. Deacon, D. Tunaley, R. N. M. Smith, *J. Organomet. Chem.*, **144**, 111 (1978).
8. E. C. Taylor, A. H. Katz, S. I. Alvarado, A. McKillop, *J. Organomet. Chem.*, **285**, C9 (1985).
9. G. B. Deacon, D. Tunaley, *J. Fluorine Chem.*, **15**, 85 (1980).
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11. G. B. Dillon, R. N. M. Smith, *Aust. J. Chem.*, **35**, 1587 (1982).

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5.3.6.3.5. by Addition of Tl(III) Salts to Olefins (Oxythallation).

Monoalkylthallium(III)s are formed at RT by treatment of olefins with Tl(III) salts (oxythallation). However, these Tl compounds undergo spontaneous decomposition. Although the oxythallation–dethallation has^{1,2} important application to organic synthesis, few Tl compounds are isolable. The decomposition of the monoalkylthallium(III)s can best be prevented by use of acetate as the anion, even though Tl(III) acetate is slower to react than more ionic salts, such as Tl(III) nitrate.

Unstrained olefins undergo trans-oxythallation in MeOH to give methoxythallation adducts; e.g., 1-hexene reacts with Tl(III) acetate or trifluoroacetate in MeOH to give 2-methoxyhexylthallium diacetate³:



where X = H, F. For X = H, the product is stable in MeOH at RT for 1 week. However, for X = F, oxidative dethallation occurs rapidly ($\approx 85\%$ in 2 h). Acyclic allenes also react with Tl(III) acetate in MeOH to give stable methoxythallation products⁴.

Thallium(III) acetate reacts with strained olefins such as norbornene, norbornadiene and benzonorbornadiene in MeOH to produce the cis-exo-acetoxymethoxythallation adducts in 80–90% yields. No methoxythallation adducts are detected, even in the crude product⁵.

Dialkyl-⁶ and alkylphenylacetylenes⁷ react with Tl(III) acetate in glacial acetic acid to give the acetoxymethoxythallation products in 50–90% yield. The yield decreases with an increase in the bulk of the alkyl group. For t-butylphenylacetylene, there is no reaction even at reflux for 24 h.

Terminal alkynes also undergo reaction with Tl(III) acetate but produce the unusual bridged oxythallation adducts⁸ $(\text{AcO})\text{RC}=\text{C}(\text{TlOAc})-\text{C}(\text{TlOAc})=\text{CR}(\text{OAc})$.

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5.3. Formation of Bonds

5.3.6. Formation of Carbon—Tl Bonds

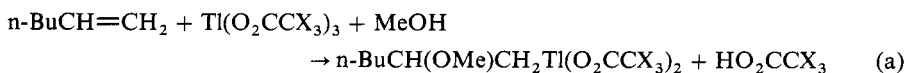
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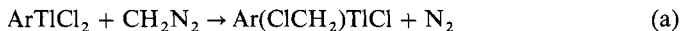
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5.3.6. Formation of Carbon—Tl Bonds

5.3.6.3. from Tl(I) or Tl(III) Salts

5.3.6.3.6. by Reaction with Diazoalkanes.

Aryl(chloromethyl)thallium chlorides, $\text{Ar}(\text{ClCH}_2)\text{TlCl}$ ($\text{Ar} = \text{Ph}$, p-tolyl), are prepared in good yields by treatment of arylthallium dichlorides with diazomethane¹:



Addition of diazomethane to ArTlCl_2 in MeOH at RT causes immediate gas evolution and precipitation of the product.

Diazomethane also reacts with Tl(III) chloride to yield² the **explosive solid** $(\text{ClCH}_2)_2\text{TlCl}$. Diazoethane reacts similarly, but no product is isolated².

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5.3.6.3.7. by Redistribution.

Monoarylthallium(III)s can undergo rearrangement in solution to the diarylthallium:



Iodides and bromides are most susceptible. For $\text{X} =$ trifluoroacetate, the reaction occurs with recrystallization from H_2O or acetone¹.

Easier and faster is reaction of arylthallium bis(trifluoroacetate) in the presence of trimethylphosphite. A rapid, exotherm results, yielding 65–95% of the diarylthallium trifluoroacetate¹. Methyl- and phenylthallium diacetates react similarly². Although the role of the trimethylphosphite is uncertain³, the synthesis is useful for diarylthallium(III)s from the accessible arylthallium(III) bis(trifluoroacetates).

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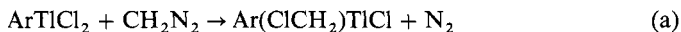
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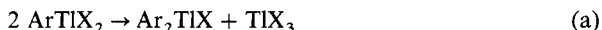
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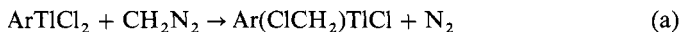
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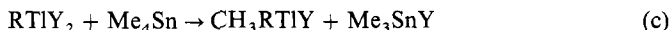
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organic derivatives of Sn^{4+} , Pb^{5+} and Bi^{4+} to produce bis(organo)thallium chlorides. The major disadvantage is the limited accessibility of the organometallics.

Organotins produce mixed diorganothallium salts from mono- or dialkyl thalliums⁶⁻⁸:



where R = Me, Et, n-propyl, phenyl; Y = isobutyrate; and:



where R = Me, Et; R' = phenyl, p-tolyl, $\text{C}_6\text{H}_5\text{C}\equiv\text{C}$, $\text{CH}_2=\text{CH}$; Y = isobutyrate; Y' = isobutyrate, OCH_3 . Tetramethyltin produces stable diorganothalliums from unstable monoalkylthallium products of oxythallation⁹.

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5.3.6.3.9. by Decarboxylation or Desulfination.

Thermal decomposition of bis(polyfluorophenyl)thallium(III) polyfluorobenzoates in boiling pyridine leads to the tris(polyfluorophenyl)thalliums¹:



The crude pyridine complex is sublimed, then treated with 1,4-dioxane to yield the tris compounds as dioxane complexes in 20–60% yield. The ease of decarboxylation is $\text{R} = \text{C}_6\text{F}_5 \geq \text{p-MeOC}_6\text{F}_4 > \text{p-HC}_6\text{F}_4 = \text{m-HC}_6\text{F}_4 \gg \text{o-HC}_6\text{F}_4$. Two ortho-fluorine atoms are required for the reaction to proceed.

In desulfination of Tl sulfonates²⁻⁴, bis(polyfluorophenyl)thallium(III) bromide reacts⁴ with the corresponding Ba polyfluorobenzenesulfonate to give the tris(polyfluorophenyl)thallium(III):



Workup is the same as with decarboxylation.

Unlike decarboxylation, desulfination does not require two ortho-fluorine atoms, although the crude products are less pure than in decarboxylation.

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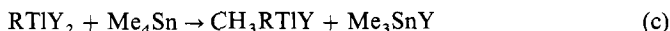
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4. R. J. Phillips, G. B. Deacon, *Aust. J. Chem.*, 32, 2381 (1979).

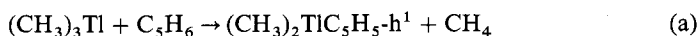
5.3. Formation of Bonds
 5.3.7. Formation of Si—Boron Bonds
 5.3.7.1. from the Elements

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5.3.6.4. from Other Organothalliums

5.3.6.4.1. by Substitution of Acidic Carbon—Hydrogen Bonds by Carbon—Tl Bonds.

Trimethylthallium reacts with acidic C—H bonds to form C—Tl bonds; e.g., Me₃Tl reacts with cyclopentadiene at RT to give quantitative yields of the mixed compound, dimethylthallium cyclopentadiene¹:



Trimethylthallium¹ or (CH₃)₂TlHN₂² also react with alkynes to produce dimethyl-ethynylthalliums, (CH₃)₂TlC≡CR, where R = H, Me, phenyl.

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Triphenylthallium reacts with n-BuLi to produce¹ n-Bu₃Tl and PhLi.

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Other routes to metal borides meet with limited success applied to the Si–B system. Silicon reduction of B₂O₃ at 1100°C produces⁹ B₄Si, whereas SiO₂ and boron at 1100–1800°C is more complex⁴ and yields¹⁰, inter alia, B₆Si. Mixtures including¹¹ B_{20–50}Si, B₁₆Si, B₈Si and B₃Si result from the thermal decomposition of boron halides onto SiC substrates under H₂; fusion electrolysis of KBF₄, KF and K₂SiF₆ also leads to combinations of product depending on the composition of the melt¹².

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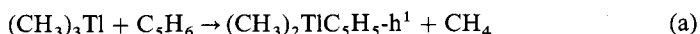
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5.3.7.2. from Dihalosilylenes by Boron Halides

Dihalosilylenes (SiX_2 , $\text{X} = \text{F}, \text{Cl}$), generated in situ from SiX_4 and elemental Si at ca. 1200°C , can be co-condensed at 77 K with boron halides to yield mixtures of silylated haloboranes (Table 1); e.g., SiF_2 and BF_3 gases are co-condensed¹ at 77 K over a 2-h period, after which unwanted volatiles (SiF_4 and BF_3) are pumped off. Trap to trap distillation separates Si_2BF_7 (-48° to -59°C), Si_3BF_9 (-18° to -28°C), $\text{Si}_4\text{BF}_{11}$ and $\text{Si}_5\text{BF}_{13}$ (-10° to $+5^\circ\text{C}$).

Mixtures of SiCl_2 and BCl_3 yield the simplest product², $\text{Cl}_3\text{SiBCl}_2$, rather than more silylated derivatives; this is in contrast to the corresponding reaction between fluorides, in which F_3SiBF_2 is rarely observed³, more complex products being the norm^{1,3,4}.

When the products of the reaction between SiF_4 and boron in a graphite tube at 1800° – 2000°C warm to RT, $\text{F}_2\text{Si}(\text{BF}_2)_2$ is formed in 5% yield⁴.

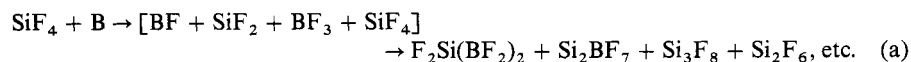


TABLE 1. REACTIONS OF DIHALOSILYLENES WITH BORON HALIDES.

Dihalosilylene	Boron halide	Time (min)	Products	Yield (%)	Ref.
SiF_2	BF_3	30	F_3SiBF_2 $\text{F}_3\text{Si}(\text{SiF}_2)\text{BF}_2$ $\text{F}_3\text{Si}(\text{SiF}_2)_2\text{BF}_2$	^a	3
SiF_2	BF_3 ^b	120	Si_2BF_7 ^c Si_3BF_9 ^d $\text{Si}_4\text{BF}_{11}$, $\text{Si}_5\text{BF}_{13}$	^e	1
SiF_2	BF_3	40	$\text{F}_3\text{Si}(\text{SiF}_2)\text{BF}_2$ $\text{F}_2\text{Si}(\text{BF}_2)_2$	5	4
SiCl_2	BCl_3 ^f	30	$\text{Cl}_3\text{SiBCl}_2$		2

^a 1.5 mmol produced per run.

^b $\text{SiF}_2 : \text{BF}_3$ at least 1:2.

^c $\text{F}_3\text{Si}(\text{SiF}_2)\text{BF}_2$.

^d $\text{F}_3\text{Si}(\text{SiF}_2)_2\text{BF}_2$.

^e Total yield of volatiles is 10–20% based on SiF_2 ; in relative amounts, 3:1:0.2 for compounds of increasing numbers of Si atoms (as listed).

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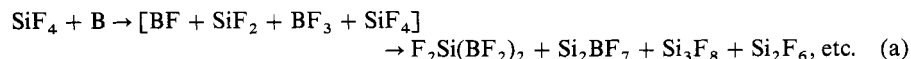


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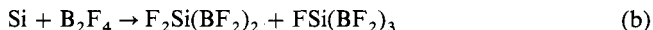
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In addition, Si atoms (produced by electron bombardment evaporation of Si) and B₂F₄ also yields FSi(BF₂)₃ in 2% yield:



Attempts to prepare inter-halogen compounds, e.g., by SiF₂ + BCl₃, are precluded by faster halogen exchange¹.

These reactions require vacuum line techniques. Vacuum lines incorporating greaseless stopcocks are preferred over those greased with Kel-F or Apiezon N; silicone grease reacts rapidly and must be avoided.

Many of the compounds produced by these procedures are pyrophoric.

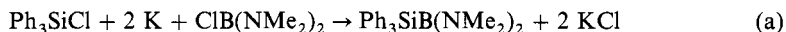
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5.3.7.3.1. with Haloboranes and Potassium Metal.

Triorganochlorosilanes and haloboranes can be coupled by potassium¹ or its sodium alloy² to yield Si—boron bonds:



Reaction (b) affords the desired compound in 27% yield, in addition to Me₆Si₂, B(NMe₂)₃ and B₂(NMe₂)₄ byproducts². **Me₃SiB(NMe₂)₂ is pyrophoric.**

Alkoxysilyl bromides, (RO)₃SiBr (R = i-Pr, t-Bu), also take part in coupling reactions of this type, yielding (RO)₃SiBNR'₂ (R = CH₃, —CH₂—) in ca. 30% yield³.

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Borane or carborane anions and Si halides form the Si—boron bond in >50% yield¹.

Deprotonation of B₃H₉ by n-BuLi forms the [B₃H₈][−] anion, which can displace chloride from chlorosilanes to yield products in which X₃Si (X = H, Me, Et) replaces a bridging hydrogen in the nido cluster². Longer reaction times are required for higher boranes³.

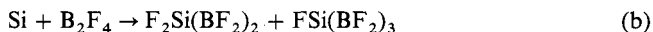
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In addition, Si atoms (produced by electron bombardment evaporation of Si) and B_2F_4 also yields $FSi(BF_2)_3$ in 2% yield:



Attempts to prepare inter-halogen compounds, e.g., by $SiF_2 + BCl_3$, are precluded by faster halogen exchange¹.

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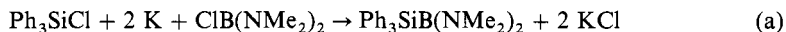
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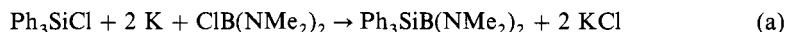
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Triorganochlorosilanes and haloboranes can be coupled by potassium¹ or its sodium alloy² to yield Si—boron bonds:



Reaction (b) affords the desired compound in 27% yield, in addition to Me_6Si_2 , $B(NMe_2)_3$ and $B_2(NMe_2)_4$ byproducts². **$Me_3SiB(NMe_2)_2$ is pyrophoric.**

Alkoxy silyl bromides, $(RO)_3SiBr$ ($R = i\text{-Pr, } t\text{-Bu}$), also take part in coupling reactions of this type, yielding $(RO)_3SiBNR'_2$ ($R = CH_3, -CH_2-$) in ca. 30% yield³.

(K. C. MOLLOY)

1. H. Nöth, G. Höllerer, *Angew. Chem., Int. Ed. Engl.*, **1**, 551 (1962).
2. H. Nöth, G. Höllerer, *Chem. Ber.*, **99**, 2197 (1966).
3. J. Pfeiffer, W. Maringgele, A. Melter, *Z. Anorg. Allg. Chem.*, **511**, 185 (1984).

5.3.7.3.2. with Boron Hydride Anions.

Borane or carborane anions and Si halides form the Si—boron bond in >50% yield¹.

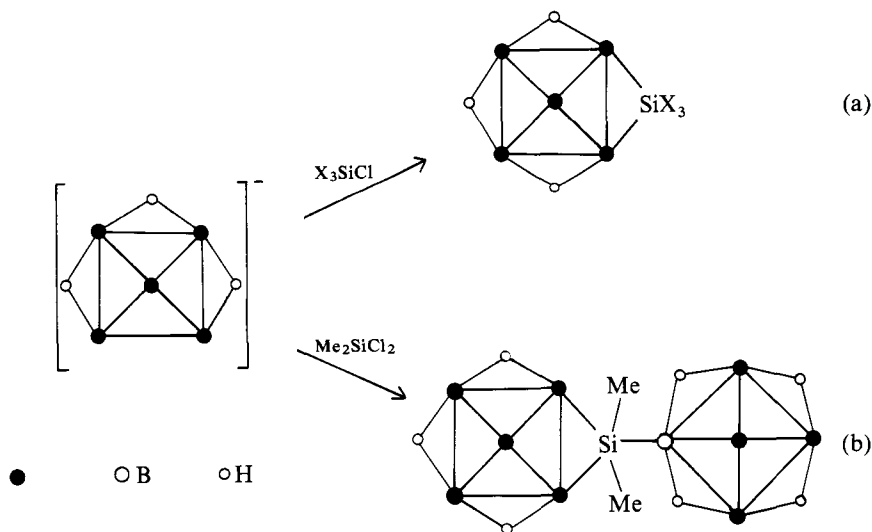
Deprotonation of B_5H_9 by $n\text{-BuLi}$ forms the $[B_5H_8]^-$ anion, which can displace chloride from chlorosilanes to yield products in which X_3Si ($X = H, Me, Et$) replaces a bridging hydrogen in the nido cluster². Longer reaction times are required for higher boranes³.

TABLE 1. BORANE ANIONS WITH SILICON HALIDES^a

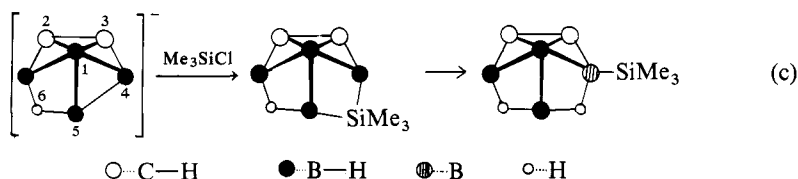
Borane anion	Silicon halide	T (°C) ^b	Time (h)	Product	Yield (%)	Ref.
[B ₅ H ₈] ^{-c}	H ₃ SiCl	-78 to -40	1½	μ-H ₃ SiB ₅ H ₈	80	2
[B ₅ H ₈] ^{-c}	Me(H)SiCl ₂	-78 to -20	2½	2,2'-(H)CH ₃ Si(B ₅ H ₈) ₂ ^d	50	4
[B ₁₀ H ₁₃] ^{-c}	Me ₃ SiCl	120 to 140	20	Me ₃ SiB ₁₀ H ₁₃	52	3
[C ₂ B ₄ H ₇] ^{-c}	H ₃ SiCl	-196 to -31	2	μ-H ₃ SiC ₂ B ₄ H ₇	60	5
[C ₂ B ₄ H ₇] ^{-c}	H ₂ SiCl ₂	0		μ,μ'-H ₂ Si(C ₂ B ₄ H ₇) ₂	70 ^f	8
[Me ₂ C ₂ B ₄ H ₅] ^{-c}	Me ₃ SiCl	-196 to 22	2	μ-Me ₃ Si(MeC) ₂ B ₄ H ₅	75	6
[4-Me ₃ SiC ₂ B ₄ H ₆] ^{-c}	Me ₃ SiCl	-196 to 25	1	μ,4-(Me ₃ Si) ₂ C ₂ B ₄ H ₆		7

^a Typical examples are chosen to illustrate scope and effectiveness.^b Reactants are mixed at the lower T and warmed to and held at the upper T over the time indicated.^c Lithium salt.^d 2-H(Me)ClSiB₅H₈ (10%) also formed.^e Sodium salt.^f Quoted as 54% in ref. 7.

More complex products ensue from dichlorosilanes, and species involving h²- and h¹-boranes are isolated⁴:



These reactions can also embrace carborane anions, e.g., anions derived from 2,3-C₂B₄H₈ and its 2,3-dimethyl derivative. Treatment of C₂B₄H₈ with NaH removes only one of the bridging protons which subsequently can be substituted by silyl groups from a chlorosilane:

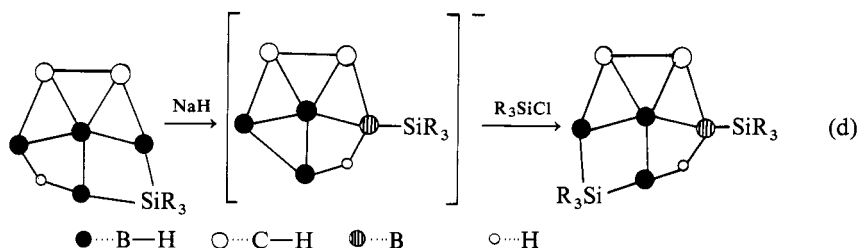


The trimethylsilyl-bridged product undergoes slow thermal rearrangement to terminal 4-Me₃SiC₂B₄H₇, or, under more forcing conditions, first to the C-substituted 2-Me₃SiC₂B₄H₇ and subsequently to the silyl-substituted closo-carborane⁵ Me₃SiC₂B₅H₆.

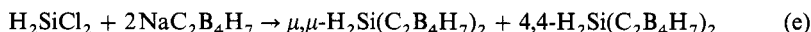
Isomerization of μ -H₃SiC₂B₄H₇ is more complex, yielding the terminally B-substituted 4-H₃SiC₂B₄H₇ at 120°C and both B-substituted 1-H₃SiC₂B₄H₇ and C-substituted 2-H₃SiC₂B₄H₇ at 220°C⁵.

Derivatives of the corresponding 2,3-dimethylcarborane, μ -X₃SiC₂(Me)₂B₄H₅, are more stable and do not isomerize⁶.

Hydride ions are capable of deprotonating 4-Me₃SiC₂B₄H₇ to yield, after subsequent reaction with Me₃SiCl, a bridged, terminal μ -4-(Me₃Si)₂C₂B₄H₆ product. The same product is obtained commencing with the bridged silylcarborane, μ -Me₃SiC₂B₄H₇, indicating a preliminary bridge-terminal rearrangement⁷:



Although μ, μ -(Me₃Si)₂C₂B₄H₆ cannot be obtained from Eq. (d), μ, μ -H₂Si(C₂B₄H₇)₂ is formed^{7,8} from H₂SiCl₂ and [C₂B₄H₇]⁻:



Equation (e) is sterically sensitive to the substituents on Si, only monobridged species being produced⁷ from analogous reactions with Me(H)SiCl₂ and (CH₃)₄SiCl₂.

Silicon tetrafluoride with [n-Bu₄N][BH₄] on an NMR scale yields [H₃BSiF₃]⁻ and [H₂B(SiF₃)₂]⁻ as [Bu₄N]⁺ salts, which could not be separated on workup⁹.

(K. C. MOLLOY)

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2. G. F. Gaines, T. V. Iorns, *J. Am. Chem. Soc.*, **90**, 6617 (1968).
3. E. Amberger, P. Leidl, *J. Organometl. Chem.*, **18**, 345 (1967).
4. D. F. Gaines, J. Ulman, *Inorg. Chem.*, **13**, 2792 (1974).
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5.3.7.4. from Silyl-Alkali-Metal Reagents

5.3.7.4.1. with Haloaminoboranes and Haloborazines and Haloboranes.

Triorganosilyl alkali-metal reagents (see §5.5.4) react with either bis-(amino)chloroboranes:



5.3. Formation of Bonds

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5.3.7. Formation of Si—Boron Bonds

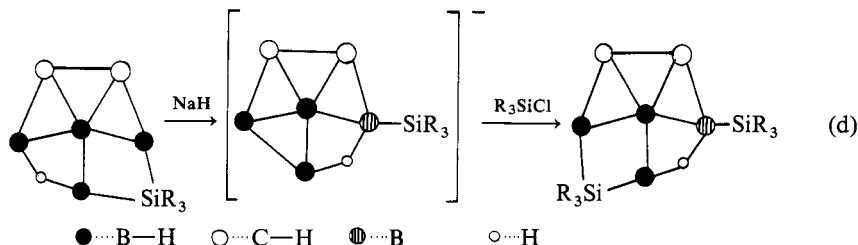
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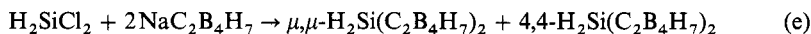
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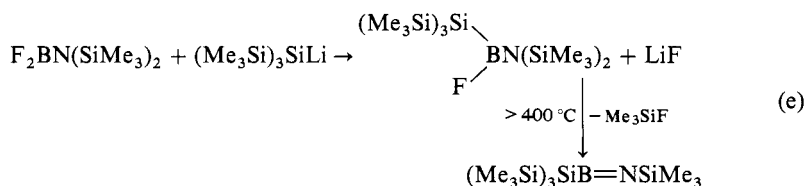
5.3.7.4. from Silyl-Alkali-Metal Reagents

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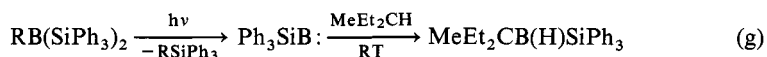
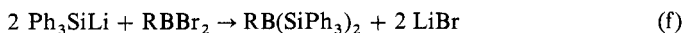
Triorganosilyl alkali-metal reagents (see §5.5.4) react with either bis-(amino)chloroboranes:



Borane	Silyl-alkali metal	T (°C) ^a	Time (h) ^a	Product	Yield (%)	Ref.
(Me ₂ N) ₂ BCl ^b	Ph ₃ SiLi	−65 to 20	2	Ph ₃ SiB(NMe ₂) ₂	67 ^c	1
Me ₂ N(n-Bu)BCl ^d	Ph ₃ SiLi	−65 to 20	2	Ph ₃ SiB(n-Bu)NMe ₂	55	1
Me ₂ NBCl ₂ ^e	(Ph ₂ Si) ₄ Li ₂ ^f	5	3	(Ph ₂ Si) ₄ BNMe ₂	26	4
Ph ₃ N ₃ B ₃ Cl ₃ ^g	Ph ₃ SiK ^h	25		Ph ₃ N ₃ B ₃ (SiPh ₃) ₃	90	7



Photolysis of $(\text{Ph}_3\text{Si})_3\text{B}$ or $\text{RB}(\text{SiPh}_3)_2$ ($\text{R} = \text{Me}$, mesityl) in 3-methylpentane at -196°C yields triphenylsilylboranediyl, which undergoes insertion on warming, e.g.¹⁰:

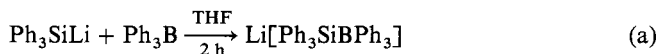


(K. C. MOLLOY)

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10. B. Pachaly, R. West, *Angew. Chem., Int. Ed. Engl.*, **23**, 454 (1984).

5.3.7.4.2. with Organoboranes.

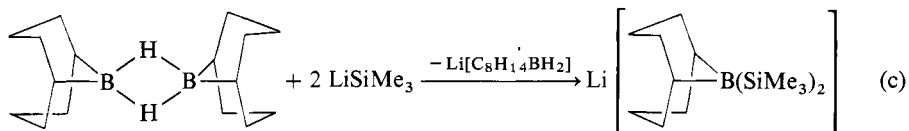
Triphenylsilyllithium (see §5.5.4) reacts with triphenylborane at RT in tetrahydrofuran (THF) to yield a 1:1 salt¹:



The product is difficult to obtain pure but can be purified by conversion to the triphenylmethylphosphonium or tetramethylammonium salts, the latter in 65% yield:



Similarly, $[(9\text{-BBN})\text{BH}]_2$, where 9-BBN is 9-borabicyclo[3.3.1]non-9-yl, reacts with Me_3SiLi :



Reactions involving more bulky silyl reagents are also known².

These reactions are precluded by excessive bulk around boron; e.g., no reaction is observed³ between $(\text{t-C}_4\text{H}_9\text{-9-BBN})\text{B}$ and LiSiMe_3 .

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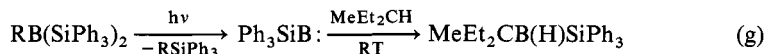
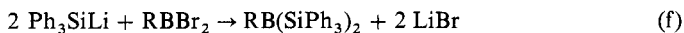
5.3. Formation of Bonds

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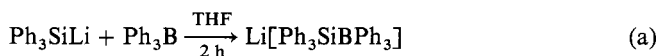


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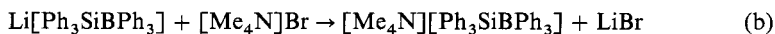
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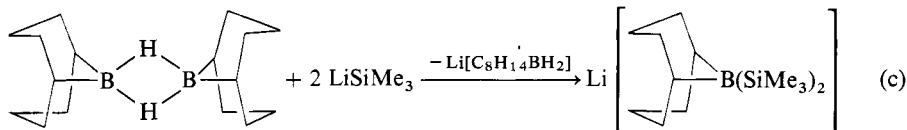
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Reactions involving more bulky silyl reagents are also known².

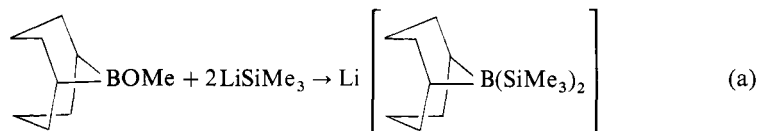
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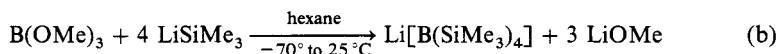
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5.3.7.4.3. with Alkoxyboranes.

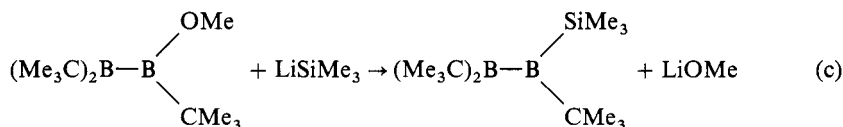
Cleavage of boron—OR bonds by organosilicon anions^{1,2} forms Si—boron bonds (cf. §5.3.7.4.2), e.g.:



In this way, tetra(organosilyl)boron anions can be derived from B(OMe)₃:



The route also yields a non-resonance stabilized (§5.3.7.4.1) silylborane³:



Complications can arise from accompanying reactions, e.g., alkyl-group transfer, hydridoborate formation and disproportionation. Thus, 2:1 Me₃SiLi and Me₂BOMe includes as products¹ Me₃B, Li[(Me₃Si)₃BMe] and Li[(Me₃Si)₂BMe₂].

Substitution on boron prior to (or in the absence of) addition that leads to salt formation only arises (1) provided the boron is not sterically or electronically shielded by its substituents, and (2) when good leaving groups are initially bonded to the metalloid. This latter parameter distinguishes reactions of alkoxyboranes from similar ones involving R₃B species in which only addition takes place¹.

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5.3.8. Formation of Si—Al Bonds**5.3.8.1. from the Elements**

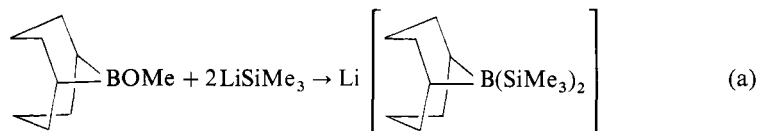
In the Al—Si system no binary compounds of the general formula Al_nSi_m are known. The system has an eutectic at 12.6% Si and 577°C; the maximum solid solubility of Si in Al is 1.65%. Commercial casting and brazing alloys vary from 5 to 20% Si in combination with other elements¹. They can be obtained by mixing the liquid elements¹.

(L. RÖSCH)

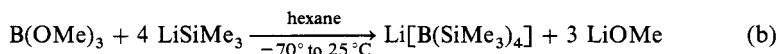
1. W. A. Anderson, W. E. Haupin, in *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 2, Wiley, New York, 1978, p. 161.

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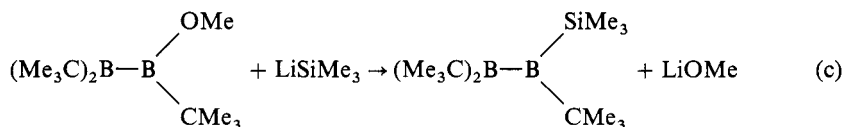
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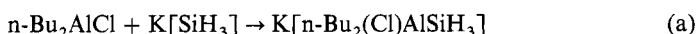
5.3. Formation of Bonds
 5.3.8. Formation of Si—Al Bonds
 5.3.8.2. from Silyl-Alkali-Metal Reagents

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5.3.8.2. from Silyl-Alkali-Metal Reagents

5.3.8.2.1. with Organoaluminum Halides.

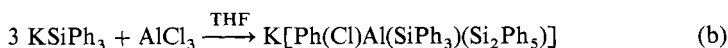
Silyl-alkali-metal reagents with Al metal and organoaluminum halides lead to silyl-Al compounds. The best results are, e.g., using $\text{K}[\text{SiH}_3]$ with $n\text{-Bu}_2\text{AlCl}$ in 1,2-dimethoxyethane (DME) at -60°C to give an alanate complex in the first step:



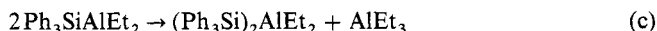
from which $n\text{-Bu}_2\text{AlSiH}_3$ can be obtained¹ by distillation at 220°C .

The H_2AlSiH_3 product is obtained² quantitatively from $\text{K}[\text{SiH}_3]$ with $\text{H}_2\text{AlCl}\cdot\text{OEt}_2$ in DME at 20°C .

Attempts to prepare $\text{Al}(\text{SiPh}_3)_3$ from KSiPh_3 and AlCl_3 fail. In liq NH_3 no compound with an Al—Si bond can be isolated. In tetrahydrofuran (THF) a potassium aluminate complex is obtained in 50% yield³:



In the first step Et_2AlBr reacts with LiSiPh_3 in THF at RT to form $\text{Ph}_3\text{SiAlEt}_2$, which redistributes:



The $(\text{Ph}_3\text{Si})_2\text{AlEt}$ is isolated⁴ as complex containing 2 mol THF and 2 mol LiBr in a yield of 60%.

Solutions of $\text{PhMe}_2\text{SiAlEt}_2$ and $\text{Li}[\text{PhMe}_2\text{SiAlMe}_3]$ form from PhMe_2SiLi with Et_2AlCl or Me_3Al . The products are not isolated, but used in situ⁵⁻⁷.

(L. RÖSCH)

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2. K. N. Semenenko, Kh. A. Taisumov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1683 (1975).
3. E. Wiberg, O. Stecher, H.-J. Andrascheck, L. Kreuzbichler, E. Staudé, *Angew. Chem., Int. Ed. Engl.*, **2**, 507 (1963).
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5. H. Hayami, M. Sato, S. Kanemoto, K. Oshima, H. Nozaki, *J. Am. Chem. Soc.*, **105**, 4491 (1983).
6. Y. Okuda, M. Sato, K. Oshima, H. Nozaki, *Tetrahedron Lett.*, 2015 (1983).
7. S. Matsubara, T. Nonaka, Y. Okuda, S. Kanemoto, K. Oshima, H. Nozaki, *Bull. Chem. Soc. Jpn.*, **58**, 1480 (1985).

5.3.8.2.2. with Lithium Aluminum Hydride or Aluminum Hydride.

In the reaction of LiSiPh_3 with LiAlH_4 in tetrahydrofuran (THF) $\text{Li}[\text{Ph}_3\text{SiAlH}_3]$ is formed:



The compound exists only in solution.

When AlH_3 is used instead, no Si—Al compound can be detected¹.

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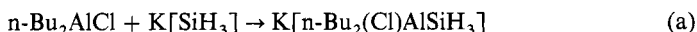
5.3. Formation of Bonds
 5.3.8. Formation of Si—Al Bonds
 5.3.8.2. from Silyl-Alkali-Metal Reagents

217

5.3.8.2. from Silyl-Alkali-Metal Reagents

5.3.8.2.1. with Organoaluminum Halides.

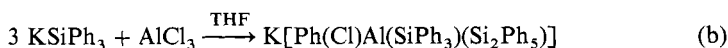
Silyl-alkali-metal reagents with Al metal and organoaluminum halides lead to silyl-Al compounds. The best results are, e.g., using $\text{K}[\text{SiH}_3]$ with $n\text{-Bu}_2\text{AlCl}$ in 1,2-dimethoxyethane (DME) at -60°C to give an alanate complex in the first step:



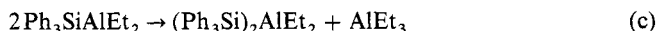
from which $n\text{-Bu}_2\text{AlSiH}_3$ can be obtained¹ by distillation at 220°C .

The H_2AlSiH_3 product is obtained² quantitatively from $\text{K}[\text{SiH}_3]$ with $\text{H}_2\text{AlCl}\cdot\text{OEt}_2$ in DME at 20°C .

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In the first step Et_2AlBr reacts with LiSiPh_3 in THF at RT to form $\text{Ph}_3\text{SiAlEt}_2$, which redistributes:



The $(\text{Ph}_3\text{Si})_2\text{AlEt}$ is isolated⁴ as complex containing 2 mol THF and 2 mol LiBr in a yield of 60%.

Solutions of $\text{PhMe}_2\text{SiAlEt}_2$ and $\text{Li}[\text{PhMe}_2\text{SiAlMe}_3]$ form from PhMe_2SiLi with Et_2AlCl or Me_3Al . The products are not isolated, but used in situ⁵⁻⁷.

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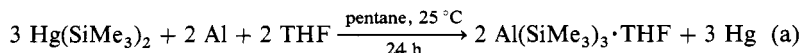
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The reaction of $\text{Hg}(\text{SiMe}_3)_2$ with Al powder in pentane and a little tetrahydrofuran (THF) gives $\text{Al}(\text{SiMe}_3)_3 \cdot \text{THF}$ in a high yield:



Side reactions occur in THF. If $\text{P}(\text{SiMe}_3)_3$ is used, the phosphine complex $(\text{SiMe}_3)_3\text{Al}-\text{P}(\text{SiMe}_3)_3$ is formed¹.

No Si—Al compound can be isolated when the reaction is run neat².

When $(\text{Me}_3\text{Si})_3\text{Al}$ is treated with tetramethylethylenediamine (TMED), $[(\text{Me}_3\text{Si})_3\text{Al}]_2 \cdot \text{TMED}$ is isolated³.

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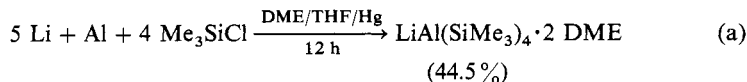
3. D. W. Goebel, Jr., J. L. Hencher, J. P. Oliver, *Organometallics*, **2**, 746 (1983).

5.3.8.4. from Organosilicon Halides with Al Metal

The best synthesis of trimethylsilyl—Al compounds is the direct reaction of Me_3SiCl with Al metal and Li in Et_2O , but tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) or their mixtures can be used.

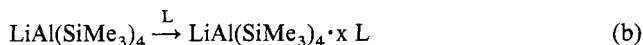
In THF, Me_3SiCl reacts with Al to form a polymer, $[\text{ClAl}(\text{SiMe}_3)\text{O}(\text{CH}_2)_4\text{SiMe}_3]_n$, which contains a Me_3Si group bonded directly to the Al chloride and silylated organic groups from the split solvent. Thus THF is attacked by trimethylsilyl—Al compounds¹.

By the reaction of Li, Al and Me_3SiCl in the presence of Hg, persilylated compounds are formed in high yields. In a mixture of boiling DME and THF, an aluminate complex is formed:



The solvated aluminate complex can be purified by sublimation at 140°C and 10^{-5} torr².

In Et_2O , $\text{LiAl}(\text{SiMe}_3)_4 \cdot x \text{ OEt}_2$ (40 %) as well as $\text{Al}(\text{SiMe}_3)_3 \cdot \text{OEt}_2$ (30 %) is formed³. The latter is soluble in pentane, but the aluminate is insoluble. When the ether-solvated aluminate complex is sublimed in vacuo, the unsolvated $\text{LiAl}(\text{SiMe}_3)_4$ is obtained. Coordinated Li aluminate complexes with a defined number of solvent molecules form² by dissolving the free complex in Et_2O , THF or DME:



where if $\text{L} = \text{Et}_2\text{O}$, $x = 3$; if $\text{L} = \text{THF}$, $x = 4$; if $\text{L} = \text{DME}$, $x = 2$. The Hg-catalyzed reaction of organosilyl halides with Al and Li is not restricted to Me_3SiCl but can be extended to other organosilyl halides also⁴.

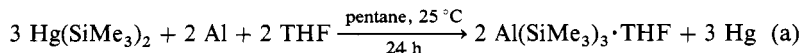
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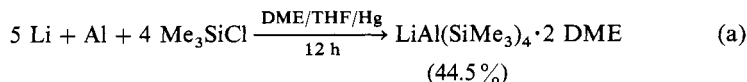
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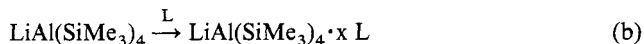
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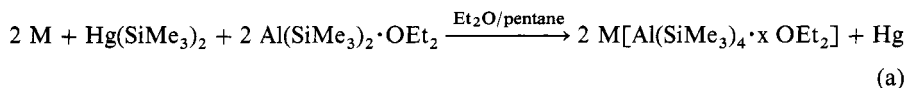
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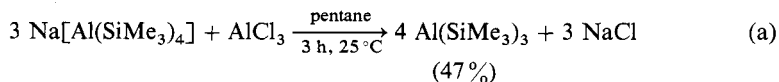
where if M = Na, x = 8 and the yield is 80 %; if M = K, x = 3, and the yield is 50 %. By sublimation of the ether complexes in vacuum, unsolvated Na[Al(SiMe₃)₄] and K[Al(SiMe₃)₄] can be isolated. By dissolving the free compounds in Et₂O, tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), the solvated aluminate complexes with a defined number of coordinated ethers are obtained¹. The solid-state structure of Na[Al(SiMe₃)₄]·2 toluene is known².

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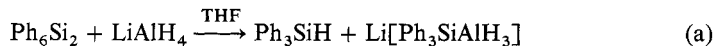


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5.3.8.7. from Disilanes or Polysilanes with LiAlH₄

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(L. RÖSCH)

5.3. Formation of Bonds

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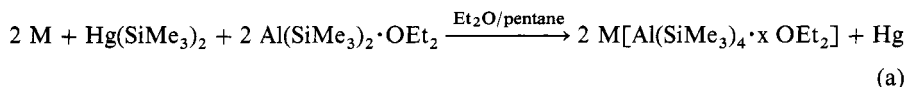
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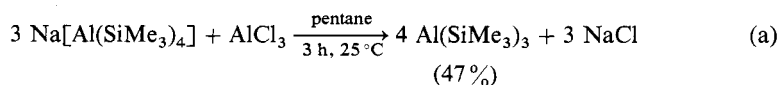


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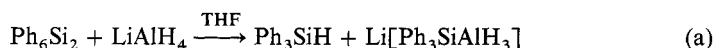
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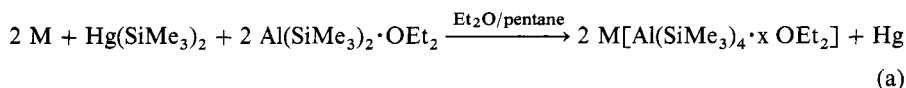
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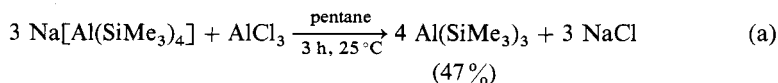


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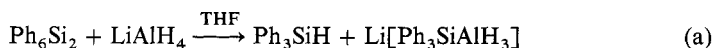
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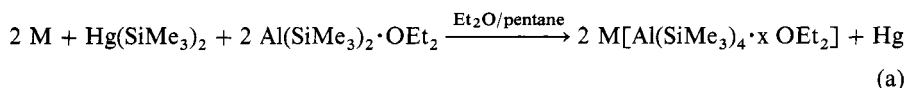
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As discussed in §5.3.8.4, Li tetrakis(trimethylsilyl)aluminate complexes are available by the Hg-catalyzed reaction of Me_3SiCl with Li metal and Al. But the analogous Na and K compounds cannot be synthesized in this direct way. These compounds are formed by:

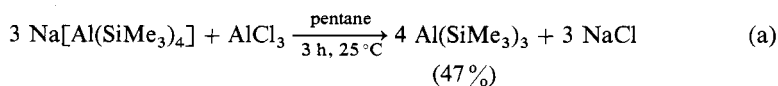


where if $\text{M} = \text{Na}$, $x = 8$ and the yield is 80%; if $\text{M} = \text{K}$, $x = 3$, and the yield is 50%. By sublimation of the ether complexes in vacuum, unsolvated $\text{Na}[\text{Al}(\text{SiMe}_3)_4]$ and $\text{K}[\text{Al}(\text{SiMe}_3)_4]$ can be isolated. By dissolving the free compounds in Et_2O , tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME), the solvated aluminate complexes with a defined number of coordinated ethers are obtained¹. The solid-state structure of $\text{Na}[\text{Al}(\text{SiMe}_3)_4] \cdot 2 \text{ toluene}$ is known².

(L. RÖSCH)

1. L. Rösch, G. Altnau, *Z. Naturforsch., Teil B*, 35, 195 (1980).2. L. Rösch, G. Altnau, C. Krüger, Y.-H. Tsay, *Z. Naturforsch., Teil B*, 38, 34 (1983).**5.3.8.6. from Alkali Tetrakis(trimethylsilyl)aluminate with Al Chloride**

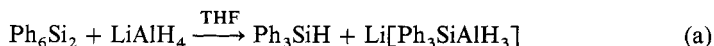
Unsolvated $\text{Al}(\text{SiMe}_3)_3$ can be made neither by the direct route, the Hg-catalyzed reaction of Me_3SiCl with Al and Li, nor by reacting $\text{Hg}(\text{SiMe}_3)_2$ with Al metal. Neither can the coordinated ether be removed from $\text{Al}(\text{SiMe}_3)_3$ solvated with Et_2O or tetrahydrofuran (THF). This product forms only by the reaction of alkali tetrakis(trimethylsilyl)aluminate with AlCl_3 in pentane¹:



(L. RÖSCH)

1. L. Rösch, G. Altnau, *J. Organomet. Chem.*, 195, 47 (1980).**5.3.8.7. from Disilanes or Polysilanes with LiAlH_4**

The reductive cleavage of phenyl-substituted organodisilanes or polysilanes produces intermediate organosilyl-Al compounds:



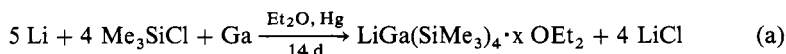
At least one aryl group must be bonded to Si. The products exist only in solution^{1,2}.

(L. RÖSCH)

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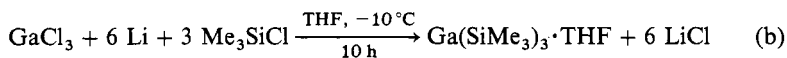
5.3.9. Formation of the Si—Ga Bond

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Heating fails to accelerate the reaction, decomposition occurring instead. On vacuum sublimation the complex undergoes partial decomposition to a colorless, pentane-insoluble fraction, $\text{LiGa}(\text{SiMe}_3)_4 \cdot 3 \text{ OEt}_2$, and to $\text{Ga}(\text{SiMe}_3)_3$ which is soluble in pentane¹.

Attempts to prepare $\text{Ga}(\text{SiMe}_3)_3$ from Ga and $\text{Hg}(\text{SiMe}_3)_3$ are unsuccessful, but good yields can be obtained by:



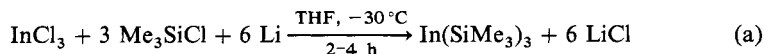
The THF adduct loses the solvent on vacuum sublimation¹.

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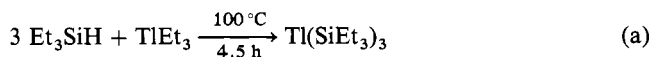
(L. RÖSCH)

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(L. RÖSCH)

5.3. Formation of Bonds

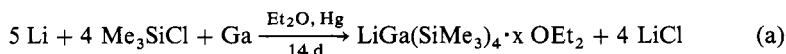
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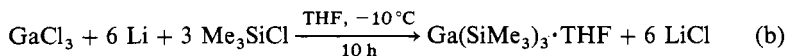
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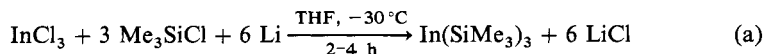
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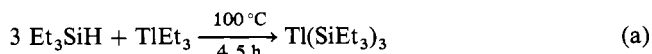


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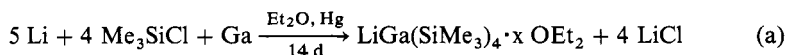


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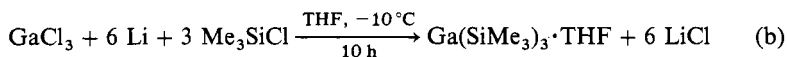
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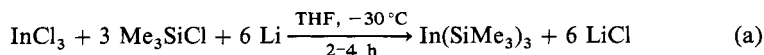
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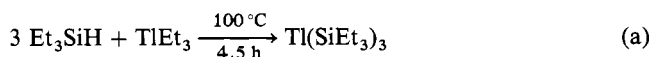
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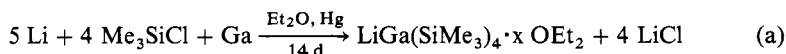


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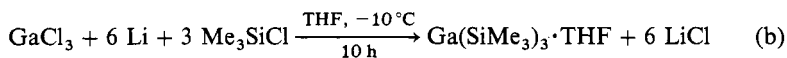
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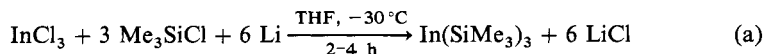
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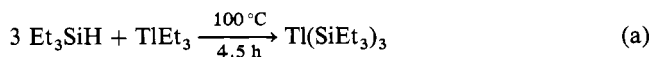
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5.3.12. Formation of the Ge—Boron Bond

5.3.12.1. from the Elements

Germanium borides are less well known than the corresponding Si compounds (see §5.3.7.1). Five conventional routes to metal borides all fail to produce a Ge boride or a solution of boron in Ge. These are: (1) reduction of GeO_2 with boron, (2) reduction of a boron- GeO_2 mixture with H_2 , (3) reduction of a B_2O_3 - GeO_2 mixture with carbon, (4) reduction of a similar mixture with B_4C and (5) direct reaction of the two elements¹. Formation of Ge borides is improbable in view of the high second ionization potential for Ge, although the possible existence of a boron germanide is suggested² (cf. §5.3.7.1).

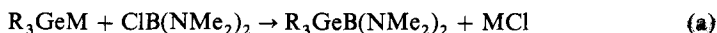
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5.3.12.2. from Germyl-Alkali Metal Reagents

5.3.12.2.1. with Haloaminoboranes and Haloborazines.

Germyl- and triorganogermyl-alkali metal reagents (see §5.5.5) react with haloaminoboranes to yield germyl-substituted aminoboranes^{1,2}:



where if $\text{R} = \text{H}$, $\text{M} = \text{K}^1$; if $\text{R} = \text{Me}$, $\text{M} = \text{Li}^2$.

The germylpotassium reaction is run in ethylene glycol at -60°C , and the product (66%) is isolated by cold trap fractionation (-20° and -196°C)¹.

As with the corresponding route to silylaminoboranes (see §5.3.7.4.1), the reaction cannot be extended to include haloalkylboranes. Thus, no identifiable germylborane can

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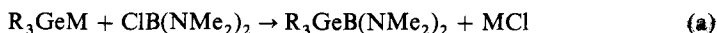
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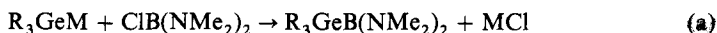
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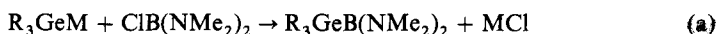
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5.3.12.2. from Germyl-Alkali Metal Reagents**5.3.12.2.1. with Haloaminoboranes and Haloborazines.**

Germyl- and triorganogermyl-alkali metal reagents (see §5.5.5) react with haloaminoboranes to yield germyl-substituted aminoboranes^{1,2}:



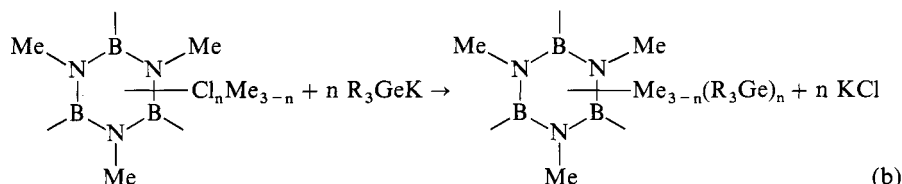
where if $\text{R} = \text{H}$, $\text{M} = \text{K}^1$; if $\text{R} = \text{Me}$, $\text{M} = \text{Li}^2$.

The germylpotassium reaction is run in ethylene glycol at -60°C , and the product (66%) is isolated by cold trap fractionation (-20° and -196°C)¹.

As with the corresponding route to silylaminoboranes (see §5.3.7.4.1), the reaction cannot be extended to include haloalkylboranes. Thus, no identifiable germylborane can

be recovered from Ph_3GeNa and $n\text{-Bu}_2\text{BCl}$, even though 90% of the chlorine can be recovered as NaCl ³.

Germyl anions can also displace chloride from chloroborazines as in Eq. (b):



where $n = 1\text{--}3$ and $\text{R} = \text{H}$ or Ph at -10°C ($\text{R} = \text{H}$) or 20°C ($\text{R} = \text{Ph}$) in $>75\%$ yield⁴.

(K. C. MOLLOY)

1. E. Amberger, R. Römer, *Z. Naturforsch., Teil B*, 23, 560 (1968).

2. H. Nöth, G. Schmid, *Allg. Prakt. Chem.*, 17, 610 (1966).

3. R. B. Booth, C. A. Kraus, *J. Am. Chem. Soc.*, 74, 1415 (1952).

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5.3.12.2.2. with Triorganoboranes.

Complex salts incorporating germylborane anions are obtained from germyl anions and R_3B :



where $\text{M} = \text{Li}$ or K . With germylpotassium, the borane is condensed onto $\text{K}[\text{Gett}_3]$ in frozen 1,2-dimethoxyethane (DME) or dimethoxyethylene glycol (glyme) (-196°C) and warmed to $0\text{--}25^\circ\text{C}$. The complex salt remains after removal of unwanted volatiles in vacuo^{1,2}, in $\approx 80\%$ yield for $\text{K}[\text{H}_3\text{GeBH}_3]$ ¹ (Table 1).

Less volatile boranes, such as Ph_3B , can be reacted at RT, but the products hydrolyze in air and are difficult to purify^{3,4}; $\text{Li}[\text{Ph}_3\text{GeBPh}_3]$ is purified by conversion to the $[\text{MePPh}_3]^+$ or $[\text{Me}_4\text{N}]^+$ salt³.

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TABLE 1. SALT FORMATION^a FROM TRIORGANOBORANES AND GERMYL-ALKALI METAL REAGENTS

R	R'	M	T ($^\circ\text{C}$)	Product	Yield (%)	Ref.
H	H	K	-196 to 25	$\text{K}[\text{H}_3\text{GeBH}_3]$	80	1
Me	H	K	-196 to 0	$\text{K}[\text{H}_3\text{GeBMe}_3]$		2
Ph	Ph	Li	25	$\text{Li}[\text{Ph}_3\text{GeBPh}_3]$	65 ^b	3
Ph	Et	Li		$\text{Li}[\text{Et}_3\text{GeBPh}_3]^\text{c}$		4

^a According to Eq. (a).

^b Isolated in pure form as $[\text{Me}_4\text{N}][\text{Ph}_3\text{GeBPh}_3]$.

^c Isolated as $\text{Li}[\text{Et}_3\text{GeBPh}_3] \cdot 4\text{HMPA}$ (hexamethylphosphoramide) from reaction in $(\text{Me}_2\text{N})_3\text{P}$ (HMPA).

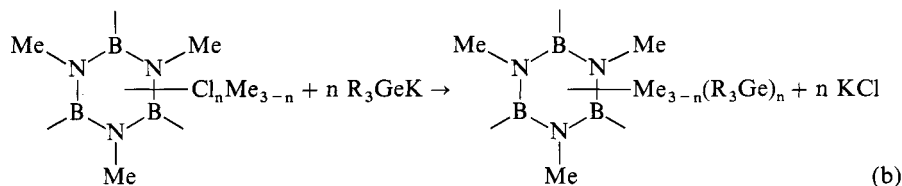
5.3. Formation of Bonds

5.3.12. Formation of the Ge—Boron Bond

5.3.12.2. from Germyl—Alkali Metal Reagents

be recovered from Ph_3GeNa and $n\text{-Bu}_2\text{BCl}$, even though 90% of the chlorine can be recovered as NaCl ³.

Germyl anions can also displace chloride from chloroborazines as in Eq. (b):



where $n = 1\text{--}3$ and $\text{R} = \text{H}$ or Ph at -10°C ($\text{R} = \text{H}$) or 20°C ($\text{R} = \text{Ph}$) in $>75\%$ yield⁴.

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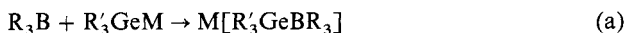
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Me	H	K	-196 to 0	$\text{K}[\text{H}_3\text{GeBMe}_3]$		2
Ph	Ph	Li	25	$\text{Li}[\text{Ph}_3\text{GeBPh}_3]$	65 ^b	3
Ph	Et	Li		$\text{Li}[\text{Et}_3\text{GeBPh}_3]^c$		4

^a According to Eq. (a).

^b Isolated in pure form as $[\text{Me}_4\text{N}][\text{Ph}_3\text{GeBPh}_3]$.

^c Isolated as $\text{Li}[\text{Et}_3\text{GeBPh}_3] \cdot 4\text{HMPA}$ (hexamethylphosphoramide) from reaction in $(\text{Me}_2\text{N})_3\text{P}$ (HMPA).

5.3. Formation of Bonds

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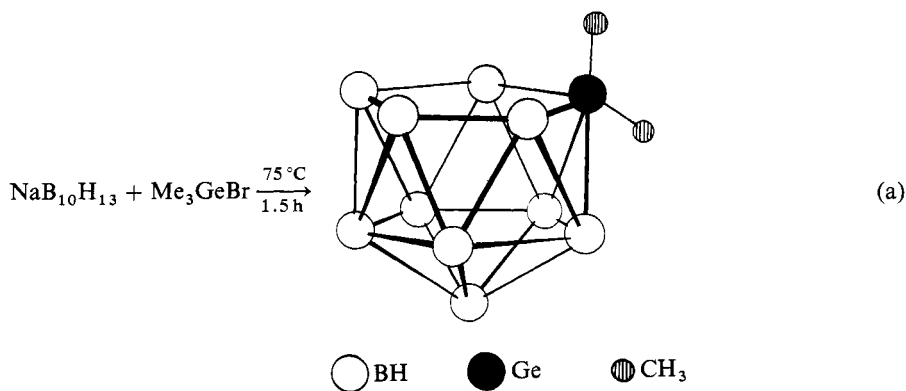
5.3.12. Formation of the Ge—Boron Bond

5.3.12.3. from Ge Halides and Boron Hydride Anions

5.3.12.3. from Ge Halides and Boron Hydride Anions

The most versatile route to Ge—boron-containing species is from Ge halides and boron hydride anions, products embracing both oxidation states of Ge, inorganic and mono-, di-, and triorganogermeryl derivatives, as well as borane and carborane substrates (Table 1) (cf. §5.3.7.3.2 for the analogous Si-based reactions).

Simple borane anions, e.g., $[\text{B}_5\text{H}_8]^-$ react with di- and triorganogermeryl chloride to yield, $\text{R}_2\text{Ge}(\text{B}_5\text{H}_8)_2$ ¹ and $\text{R}_3\text{GeB}_5\text{H}_8$ ², respectively, in high ($\approx 75\%$) yield for the tri- but reduced ($\approx 20\%$) for the di-organogermeryl boranes. With higher boranes more complex reactions result in low yields of unexpected products; e.g., Me_3GeBr and $\text{B}_{10}\text{H}_{13}$ produce $\text{Me}_2\text{GeB}_{10}\text{H}_{12}$ in $\approx 5\%$ yield, in which Ge formally replaces two bridging hydrogens in $\text{B}_{10}\text{H}_{14}$ by insertion into the cage framework, to release CH_4 ³:

TABLE 1. GERMANIUM HALIDES WITH BORON HYDRIDE ANIONS^a

Anion	Halide	T (°C) ^b	Time (h) ^b	Product	Yield (%)	Ref.
$[\text{B}_5\text{H}_8]^-$ ^c	H_3GeCl	−78 to −22	1½	$\text{H}_3\text{GeB}_5\text{H}_8$	74	2
$[\text{B}_5\text{H}_8]^-$ ^c	Me_2GeCl_2	−65 to −30	2½	$\text{Me}_2\text{Ge}(\text{B}_5\text{H}_8)_2$ ^d	20	1
$[\text{B}_{10}\text{H}_{13}]^-$ ^c	Me_3GeBr	75	1½	$\text{Me}_2\text{GeB}_{10}\text{H}_{12}$	5	3
$[\text{C}_2\text{B}_4\text{H}_7]^-$ ^c	Me_3GeCl	−196 to 25	1	$\text{Me}_2\text{GeC}_2\text{B}_4\text{H}_7$	70	4
$[\text{C}_2\text{B}_4\text{H}_7]^-$ ^c	H_3GeCl	−196 to 0	½	$\text{H}_3\text{GeC}_2\text{B}_4\text{H}_7$	2	4
$[(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)\text{FeH}]^-$ ^c	GeI_2	−196 to 0	1	$\text{GeFe}[\text{Me}_2\text{C}_2\text{B}_4\text{H}_4]_2$	12	11
$[\text{CHB}_9\text{H}_9\text{P}]^{2-}$	GeI_2	75	15–24 ^f	$\text{GeCHB}_9\text{H}_9\text{P}$	68 ^g	12
$[\text{B}_9\text{C}_2\text{H}_{11}]^{2-}$ ^c	GeI_2	80	24	$\text{GeC}_2\text{B}_9\text{H}_{11}$	30	9
$[\text{CB}_{10}\text{H}_{11}]^{3-}$ ^c	MeGeCl_3	67		$\text{MeGeCB}_{10}\text{H}_{11}$	—	7

^a Reactions chosen to illustrate the scope of reagent combinations and yield limitations.

^b Low-T reactions require mixing of reagents at the lowest T, then warming to and holding at the higher T over the indicated time.

^c Lithium salt.

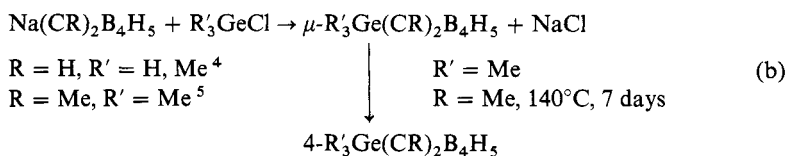
^d Mixture of 2,2' and μ , 2 isomers.

^e Sodium salt.

^f Reaction times vary with phosphacarborane anion used.

^g Yield of 3,2,1-GePCHB₉H₉ from $[\text{7,8-PCHB}_9\text{H}_9]^{2-}$.

Carboranes and the corresponding C-methylated species ($R = H, Me$, respectively) undergo a parallel series of reactions:



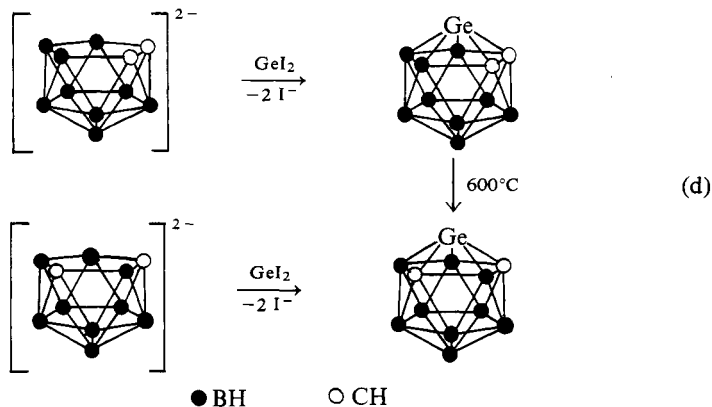
Germyl halides are less effective than organogermanium halides (see Table 1). Bridge-terminal rearrangements occur, in contrast to Si compounds, where no such isomerization is observed in the C-methylated carborane derivatives (see §5.3.7.3.2). Further reduction with NaH to yield $[4\text{-R}_3\text{Ge}(\text{CH})_2\text{B}_4\text{H}_4]^-$ is less facile than for the Si analogues⁶ (only 30% of the expected H_2 is liberated), inhibiting further germylation of the cluster.

Carborane derivatives of monoorganogermanes can also be synthesized⁸:

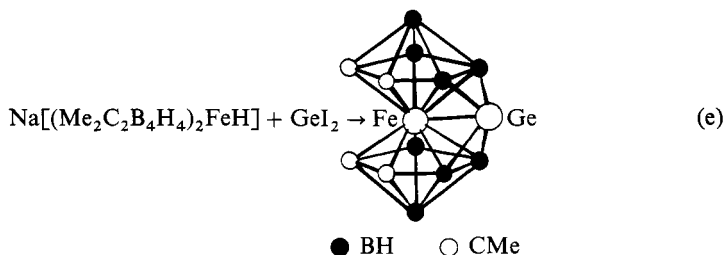


Derivatives of divalent Ge can be obtained⁹⁻¹² from carborane anions and GeI_2 , although long times (15–54 h at solvent reflux) are usually necessary.

Two isomers of $\text{closo-GeC}_2\text{B}_9\text{H}_{11}$ are obtained from nido-7,8- and $[7,9\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$, the 3,1,2- $\text{GeC}_2\text{B}_9\text{H}_{11}$ derivative undergoing thermal rearrangement^{9,10} to 3,1,7- $\text{GeC}_2\text{B}_9\text{H}_{11}$ at 600°C :



Germanium can also be inserted into ferra-¹¹, phospho-¹² and arsenacarboranes¹² by reaction of GeI_2 with the appropriate heterocarborane anion:



Reactions involving the group-V carboranes follow Eq. (d), in which carbon is replaced by either P or As in the cage.

(K. C. MOLLOY)

1. D. F. Gaines, J. Ulman, *Inorg. Chem.*, **13**, 2792 (1974).
2. D. F. Gaines, T. V. Iorns, *J. Am. Chem. Soc.*, **90**, 6617 (1968).
3. R. E. Loffredo, A. D. Norman, *J. Am. Chem. Soc.*, **93**, 5587 (1971).
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6. A. Tabereaux, R. N. Grimes, *Inorg. Chem.*, **12**, 792 (1973).
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8. G. S. Wikholm, L. J. Todd, *J. Organomet. Chem.*, **71**, 219 (1974).
9. R. W. Rudolph, R. L. Voorhees, R. E. Cochoy, *J. Am. Chem. Soc.*, **92**, 3351 (1970).
10. V. Chowdry, W. Pretzer, D. N. Rai, R. W. Rudolph, *J. Am. Chem. Soc.*, **95**, 4560 (1973).
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5.3.13. Formation of the Ge—Al Bond

5.3.13.1. from the Elements

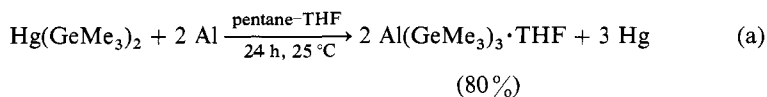
In the Al–Ge system no binary compounds of the general formula Al_nGe_m are known. The system has a eutectic at 30.3 at % Ge and 423°C^{-1} . Alloys of Ge and Al are of little importance².

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5.3.13.2. from Bis(germyl)mercurials with Al Metal

By reaction of $\text{Hg}(\text{GeMe}_3)_2$ with Al metal in pentane with a trace of tetrahydrofuran (THF), the only known alkylgermyl–Al compound, $\text{Al}(\text{GeMe}_3)_3 \cdot \text{THF}$, is formed in high yield¹:



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5.3. Formation of Bonds

225

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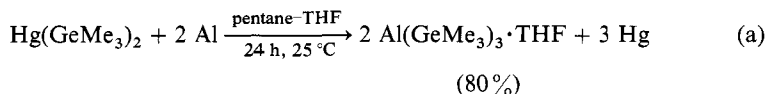
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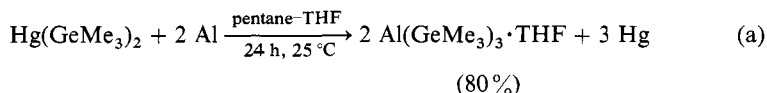
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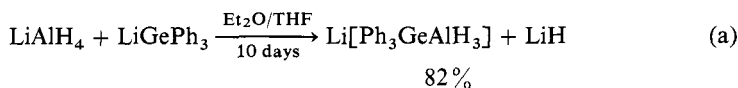
226 5.3. Formation of Bonds

5.3.13. Formation of the Ge—Al Bond

5.3.13.5. from Ge Halides or Organogermanium Halides with Al Alkyls

5.3.13.3. from Germyl-Alkali Metal Reagent with Lithium Aluminum Hydride

When LiAlH_4 is reacted with LiGePh_3 in tetrahydrofuran (THF)/ Et_2O at RT, $\text{Li}[\text{Ph}_3\text{GeAlH}_3]$ is formed:



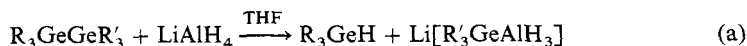
The compound is isolated¹ with coordinated THF.

(L. RÖSCH)

1. N. Duffaut, J. Dunogues, R. Calas, J. Gerval, P. Riviere, J. Satgé, A. Cazes, *J. Organomet. Chem.*, **149**, 57 (1978).

5.3.13.4. from Aryldigermanes by Reaction with Lithium Aluminum Hydride

Reduction of aryldigermanes by LiAlH_4 in tetrahydrofuran (THF) leads, in high yields, to the corresponding hydrogermanes via Li germylaluminates:



The Al-Ge compounds $\text{Li}[\text{R}_3\text{GeAlH}_3]$ (with $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2$) exist only in solution; their composition is proved by reaction and for $\text{Li}[\text{Ph}_3\text{AlH}_3]$, by comparison with the compound synthesized as shown, in §5.3.13.3¹.

(L. RÖSCH)

1. N. Duffaut, J. Dunogues, R. Calas, J. Gerval, P. Riviere, J. Satgé, A. Cazes, *J. Organomet. Chem.*, **149**, 57 (1978).

5.3.13.5. from Ge Halides or Organogermanium Halides with Al Alkyls

To account for the formation of digermanes in the alkylation of GeCl_4 with AlMe_3 , AlEt_3 , $\text{Al}(\text{Bu}-i)_3$ and $\text{Me}_3\text{Al}_2\text{Cl}_3$, the formation of reactive Ge-Al compounds is postulated, but no isolation or characterization of these intermediates is possible¹.

(L. RÖSCH)

1. F. Glockling, J. R. C. Light, *J. Chem. Soc., A*, 623 (1967).

5.3.14. Formation of the Ge—Ga Bond

The Ge-Ga compounds $\text{Ga}(\text{GeEt}_3)_3$ and $\text{BrGa}(\text{GeEt}_3)_2$ are known¹, only by their spectral data; the preparations are not described².

(L. RÖSCH)

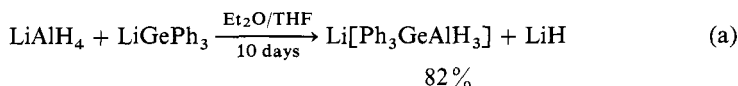
226 5.3. Formation of Bonds

5.3.13. Formation of the Ge—Al Bond

5.3.13.5. from Ge Halides or Organogermanium Halides with Al Alkyls

**5.3.13.3. from Germyl-Alkali Metal Reagent
with Lithium Aluminum Hydride**

When LiAlH_4 is reacted with LiGePh_3 in tetrahydrofuran (THF)/ Et_2O at RT, $\text{Li}[\text{Ph}_3\text{GeAlH}_3]$ is formed:



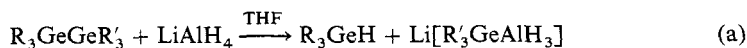
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**5.3.13.4. from Aryldigermanes by Reaction
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Reduction of aryldigermanes by LiAlH_4 in tetrahydrofuran (THF) leads, in high yields, to the corresponding hydrogermanes via Li germylaluminates:



The Al-Ge compounds $\text{Li}[\text{R}_3\text{GeAlH}_3]$ (with $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2$) exist only in solution; their composition is proved by reaction and for $\text{Li}[\text{Ph}_3\text{AlH}_3]$, by comparison with the compound synthesized as shown, in §5.3.13.3¹.

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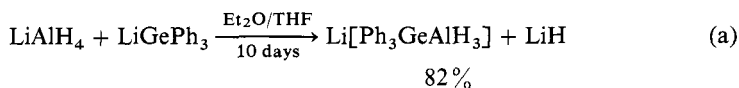
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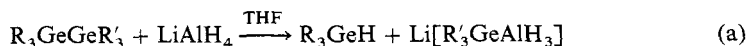
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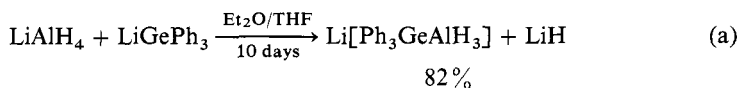
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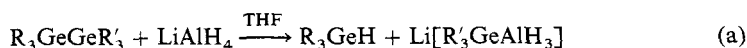
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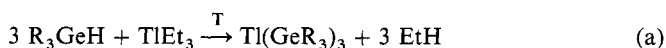
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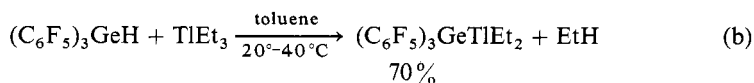
5.3.16. Formation of the Ge—Tl Bond

The Ge—Tl compounds $\text{Tl}(\text{GeEt}_3)_3$ ¹ and $\text{Tl}[\text{Ge}(\text{CH}_2\text{SiMe}_3)_3]_3$ ² can be prepared in high yields from the hydride:



where if $\text{R} = \text{Et}$ and $\text{T} = 100^\circ\text{C}$, the yield is 91–100%, and if $\text{R} = \text{Me}_3\text{SiCH}_2$ and $\text{T} = 50^\circ\text{C}$, the yield is 66.9%.

Under mild conditions, 1:1 $(\text{C}_6\text{F}_5)_3\text{GeH}$ and TlEt_3 give³ $(\text{C}_6\text{F}_5)_3\text{GeTlEt}_2$:



From 3:1 stoichiometry $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{TlEt}$ forms in 62% yield³. The polymer $[(\text{C}_6\text{F}_5)_2\text{GeTlEt}]_n$ forms³ in 66% yield from $(\text{C}_6\text{F}_5)_2\text{GeH}_2$ with TlEt_3 .

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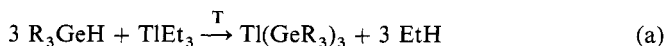
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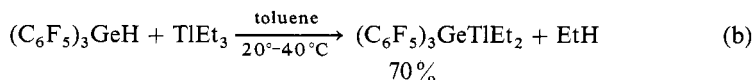
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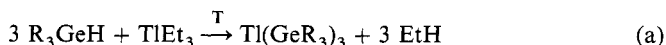
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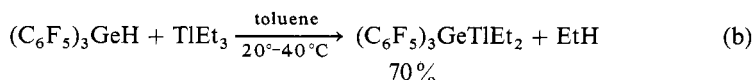
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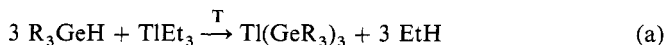
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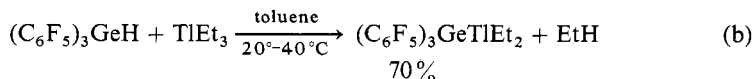
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5.3.17.2. from Stannyl-Alkali Metal Reagents

5.3.17.2.1. with Trialkylboranes.

Low-T mixing of Me_3SnLi (-20°C) and B_2H_6 (-50°C) in tetrahydrofuran (THF) yields a tin-containing borane anion¹:



The synthetic route is less well developed than for Si (see. §5.3.7.4) or Ge (see §5.3.12.2) but by analogy organostannylborane anions should be accessible.

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1. W. Biffar, H. Nöth, H. Pommerening, R. Schwerthoffer, W. Storch, B. Wrackmeyer, *Chem Ber.*, 114, 49 (1981).

5.3.17.2.2. with Haloaminoboranes.

Stannyl-alkali metal reagents and haloaminoboranes yield Sn—boron bonds, but the method does not include haloborazines as starting materials (Table 1).

Commonly, R_3SnLi displaces chloride (as LiCl) from monohalo(amino)boranes:



where $\text{R} = \text{Me}^1, \text{Et}^2$, $\text{R}' = \text{Me}, \text{Et}$ and cyclizing alkyls $(-\text{CH}_2-)_n$ ($n = 2^3, 3^4$). Derivatives of these latter cyclic diaminoboranes are more stable to O_2 than the corresponding linear amines³.

From dihalo(amino)boranes two products are possible, depending on stoichiometry. For a 1:1 ratio, only one chloride is displaced by R_3Sn :

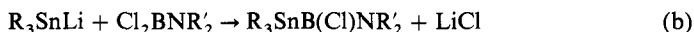


TABLE 1. ORGANOSTANNYL-ALKALI METAL REAGENTS WITH HALOAMINOBORANES

Borane	Stannyl-alkali metal ^a	T ($^\circ\text{C}$)	Time (h)	Product	Yield (%)	Ref.
$(\text{Et}_2\text{N})_2\text{BCl}$	Me_3SnLi	0	6	$\text{Me}_3\text{SnB}(\text{NEt}_2)_2$	70	1
Et_2NBCl_2	Me_3SnLi	0	6	$\text{Me}_3\text{SnB}(\text{Cl})\text{NEt}_2$	40	1
Et_2NBCl_2	Me_3SnLi^b	-60 to -30°	2	$(\text{Me}_3\text{Sn})_2\text{BNEt}_2$		1
$\text{N}(\text{CH}_2)_3\text{NBCl}$	Me_3SnLi	25	0.17	$\text{Me}_3\text{SnBN}(\text{CH}_2)_3\text{N}$	45	4
$(\text{Me}_2\text{N})_2\text{B}_2\text{Cl}_2$	Me_3SnLi^b	-78 to 67°	0.5	$(\text{Me}_3\text{Sn})_2\text{B}_2(\text{NMe}_2)_2$	70	6

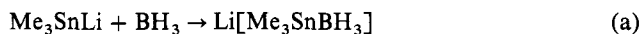
^a The reagent in tetrahydrofuran must be completely free from Li metal.

^b 2 mol equiv.

^c Reagents combined at the lower T and ultimately maintained at higher T value over the time indicated.

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Low-T mixing of Me_3SnLi (-20°C) and B_2H_6 (-50°C) in tetrahydrofuran (THF) yields a tin-containing borane anion¹:



The synthetic route is less well developed than for Si (see §5.3.7.4) or Ge (see §5.3.12.2) but by analogy organostannylborane anions should be accessible.

(K. C. MOLLOY)

1. W. Biffar, H. Nöth, H. Pommerening, R. Schwerthoffer, W. Storch, B. Wrackmeyer, *Chem Ber.*, 114, 49 (1981).**5.3.17.2.2. with Haloaminoboranes.**

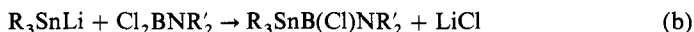
Stannyl-alkali metal reagents and haloaminoboranes yield Sn—boron bonds, but the method does not include haloborazines as starting materials (Table 1).

Commonly, R_3SnLi displaces chloride (as LiCl) from monohalo(amino)boranes:



where $\text{R} = \text{Me}^1$, Et^2 , $\text{R}' = \text{Me}$, Et and cyclizing alkyls ($-\text{CH}_2-$)_n ($n = 2^3, 3^4$). Derivatives of these latter cyclic diaminoboranes are more stable to O_2 than the corresponding linear amines³.

From dihalo(amino)boranes two products are possible, depending on stoichiometry. For a 1:1 ratio, only one chloride is displaced by R_3Sn :

**TABLE 1. ORGANOSTANNYL-ALKALI METAL REAGENTS WITH HALOAMINOBORANES**

Borane	Stannyl-alkali metal ^a	T (°C)	Time (h)	Product	Yield (%)	Ref.
$(\text{Et}_2\text{N})_2\text{BCl}$	Me_3SnLi	0	6	$\text{Me}_3\text{SnB}(\text{NEt}_2)_2$	70	1
Et_2NBCl_2	Me_3SnLi	0	6	$\text{Me}_3\text{SnB}(\text{Cl})\text{NEt}_2$	40	1
Et_2NBCl_2	Me_3SnLi^b	-60 to -30°	2	$(\text{Me}_3\text{Sn})_2\text{BNEt}_2$		1
$\text{N}(\text{CH}_2)_3\text{NBCl}$	Me_3SnLi	25	0.17	$\text{Me}_3\text{SnB}(\text{N}(\text{CH}_2)_3\text{N})$	45	4
$(\text{Me}_2\text{N})_2\text{B}_2\text{Cl}_2$	Me_3SnLi^b	-78 to 67°	0.5	$(\text{Me}_3\text{Sn})_2\text{B}_2(\text{NMe}_2)_2$	70	6

^a The reagent in tetrahydrofuran must be completely free from Li metal.^b 2 mol equiv.^c Reagents combined at the lower T and ultimately maintained at higher T value over the time indicated.

5.3. Formation of Bonds

5.3.17. Formation of the Sn—Boron Bond

5.3.17.2. from Stannyl-Alkali Metal Reagents

1. R. Thompson, *Prog. Boron Chem.*, **2**, 177 (1970).
2. J. Cueilleron, P. Pichat, *Fr. Pat.* 1,471,238 (1967); *Chem. Abstr.*, **67**, 74,972 (1967).

5.3.17.2. from Stannyl-Alkali Metal Reagents

5.3.17.2.1. with Trialkylboranes.

Low-T mixing of Me_3SnLi (-20°C) and B_2H_6 (-50°C) in tetrahydrofuran (THF) yields a tin-containing borane anion¹:



The synthetic route is less well developed than for Si (see. §5.3.7.4) or Ge (see §5.3.12.2) but by analogy organostannylborane anions should be accessible.

(K. C. MOLLOY)

1. W. Biffar, H. Nöth, H. Pommerening, R. Schwerthoffer, W. Storch, B. Wrackmeyer, *Chem. Ber.*, **114**, 49 (1981).

5.3.17.2.2. with Haloaminoboranes.

Stannyl-alkali metal reagents and haloaminoboranes yield Sn—boron bonds, but the method does not include haloborazines as starting materials (Table 1).

Commonly, R_3SnLi displaces chloride (as LiCl) from monohalo(amino)boranes:



where $\text{R} = \text{Me}^1, \text{Et}^2$, $\text{R}' = \text{Me}, \text{Et}$ and cyclizing alkyls ($-\text{CH}_2-$)_n ($n = 2^3, 3^4$). Derivatives of these latter cyclic diaminoboranes are more stable to O_2 than the corresponding linear amines³.

From dihalo(amino)boranes two products are possible, depending on stoichiometry. For a 1:1 ratio, only one chloride is displaced by R_3Sn :

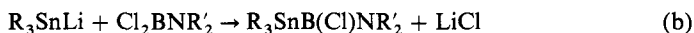


TABLE 1. ORGANOSTANNYL-ALKALI METAL REAGENTS WITH HALOAMINOBORANES

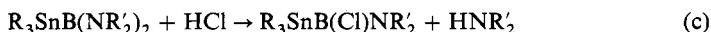
Borane	Stannyl-alkali metal ^a	T (°C)	Time (h)	Product	Yield (%)	Ref.
$(\text{Et}_2\text{N})_2\text{BCl}$	Me_3SnLi	0	6	$\text{Me}_3\text{SnB}(\text{NEt}_2)_2$	70	1
Et_2NBCl_2	Me_3SnLi	0	6	$\text{Me}_3\text{SnB}(\text{Cl})\text{NEt}_2$	40	1
Et_2NBCl_2	Me_3SnLi^b	-60 to -30°	2	$(\text{Me}_3\text{Sn})_2\text{BNEt}_2$		1
$\text{N}(\text{CH}_2)_3\text{NBCl}$	Me_3SnLi	25	0.17	$\text{Me}_3\text{SnBN}(\text{CH}_2)_3\text{N}$	45	4
$(\text{Me}_2\text{N})_2\text{B}_2\text{Cl}_2$	Me_3SnLi^b	-78 to 67°	0.5	$(\text{Me}_3\text{Sn})_2\text{B}_2(\text{NMe}_2)_2$	70	6

^a The reagent in tetrahydrofuran must be completely free from Li metal.

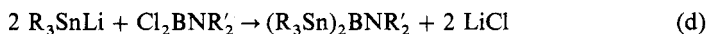
^b 2 mol equiv.

^c Reagents combined at the lower T and ultimately maintained at higher T value over the time indicated.

This stannylborane can be obtained indirectly by acidolysis of the corresponding diaminoborane¹:



If ratios in Eq. (b) are 2:1, a fully stannylated aminoborane is produced:



The route is limited by its inability to include haloalkylboranes (R_2BCl , RBCl_2 , etc.); e.g., from Ph_3SnLi and BCl_3 , RBCl_2 or R_2BCl , no tin-boron compounds are detected, Ph_6Sn_2 being the major product⁵. Compounds $\text{R}_n\text{Sn}(\text{BR}'_2)_{4-n}$ are best obtained from organoboron-Co compounds (§5.3.17.3.1).

(K. C. MOLLOY)

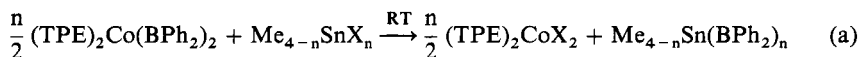
1. H. Nöth, R. Schwerthöffer, *Chem. Ber.*, **114**, 3056 (1981).
2. H. Nöth, K.-H. Hermannsdörfer, *Angew. Chem., Int. Ed. Engl.*, **3**, 377 (1964).
3. K. Niedenzu, E. F. Rothgery, *Synth. Inorg. Met.-Org. Chem.*, **2**, 1 (1972).
4. E. B. Bradley, R. H. Herber, P. J. Busse, K. Niedenzu, *J. Organomet. Chem.*, **52**, 297 (1973).
5. H. Nöth, H. Schäfer, G. Schmid, *Angew. Chem., Int. Ed. Engl.*, **8**, 515 (1969).
6. W. Biffar, H. Nöth, H. Pommerening, R. Schwerthöffer, W. Storch, B. Wrackmeyer, *Chem. Ber.*, **114**, 49 (1981).

5.3.17.3. from Tin Halides

5.3.17.3.1. with Boron-Co Compounds.

Cleavage of the boron—Co bond by tin halides yields Sn—boron bonds^{1,2}. The route supplements those involving stannyl-alkali-metal reagents and haloaminoboranes (§5.3.17.2.2).

Reactions involving orangoboron-Co compounds are:



where $\text{TPE} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, and specific examples are given in Table 1.

The reaction is quantitative in terms of $(\text{TPE})_2\text{CoX}_2$ produced and yields the stannyl borane in 60% yield after workup¹.

TABLE 1. REACTIONS BETWEEN $(\text{R}_2\text{B})_2\text{Co}(\text{TPE})_2$ ^a AND TIN HALIDES^{b,c}

R	Tin halides	Stoichiometry ^d	Product	Yield (%)
Ph	SnBr_4	2:1	$\text{Sn}(\text{BPh}_2)_4$ ^e	76
Ph	Me_2SnCl_2	1:1	$\text{Me}_2\text{Sn}(\text{BPh}_2)_2$	79
Br	MeSnCl_3	1.5:1:4	$\text{MeSn}(\text{BBr}_2)_3 \cdot 4 \text{ TPE}$ ^a	20
Br	Me_3SnCl	1:2:4	$\text{Me}_3\text{SnBBr}_2 \cdot 3 \text{ TPE}$ ^a	13

^a $\text{TPE} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

^b Reactions chosen to typify the synthetic route and refer to ca. 4 h stirring at RT.

^c Ref. 1.

^d $(\text{R}_2\text{B})_2\text{Co}(\text{TPE})_2$:tin halide:TPE (where applicable).

^e Reaction must be carried out under pure Ar or N_2 .

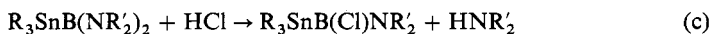
5.3. Formation of Bonds

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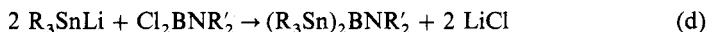
5.3.17. Formation of the Sn—Boron Bond

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(K. C. MOLLOY)

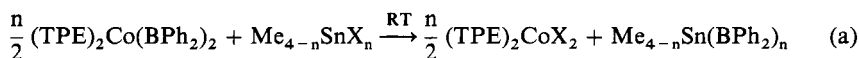
1. H. Nöth, R. Schwerthöffer, *Chem. Ber.*, **114**, 3056 (1981).
2. H. Nöth, K.-H. Hermannsdörfer, *Angew. Chem., Int. Ed. Engl.*, **3**, 377 (1964).
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The reaction is quantitative in terms of $(\text{TPE})_2\text{CoX}_2$ produced and yields the stannyl borane in 60% yield after workup¹.

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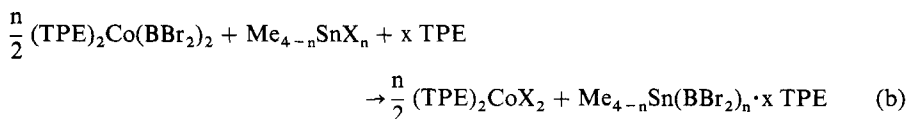
^b Reactions chosen to typify the synthetic route and refer to ca. 4 h stirring at RT.

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^d $(\text{R}_2\text{B})_2\text{Co}(\text{TPE})_2$: tin halide:TPE (where applicable).

^e Reaction must be carried out under pure Ar or N_2 .

With uncomplexed TPE, the reaction can be extended to include $\text{Me}_{4-n}\text{Sn}(\text{BBr}_2)_n \cdot \text{TPE}$, unattainable in the uncomplexed state:



The TPE required varies with organotin halide, leading to values of $x = 3$ or 4 in the final products (see Table 1)

(K. C. MOLLOY)

1. H. Nöth, H. Schäfer, G. Schmid, *Z. Naturforsch., Teil B*, 26, 497 (1971).
2. H. Nöth, H. Schäfer, G. Schmid, *Angew. Chem., Int. Ed. Engl.*, 8, 515 (1969).

5.3.17.3.2. with Boron Hydride Anions.

The scope for Sn—B bond formation is narrower than for Si (§5.7.3.2) and Ge (§5.3.12.3)¹. The reactions are complex, with Sn metal and free carborane accompanying the stannaborane as products, the latter thus being obtained in poor yield¹ (Table 1).

Lower boranes, e.g., $[\text{B}_5\text{H}_8]^-$, with Me_3SnCl give² $\mu\text{-Me}_3\text{SnB}_5\text{H}_8$, but higher boranes result in more complex reactions and concomitant low yields^{3,4}.

Similarly, $[\text{C}_2\text{B}_4\text{H}_7]^-$ and Me_3SnBr combine to give the expected⁵ $[\mu\text{-Me}_3\text{SnC}_2\text{B}_4\text{H}_7]^-$, but with SnCl_2 only low yields of the closo-stannaborane, $\text{SnC}_2\text{B}_4\text{H}_6$, are obtained⁶:

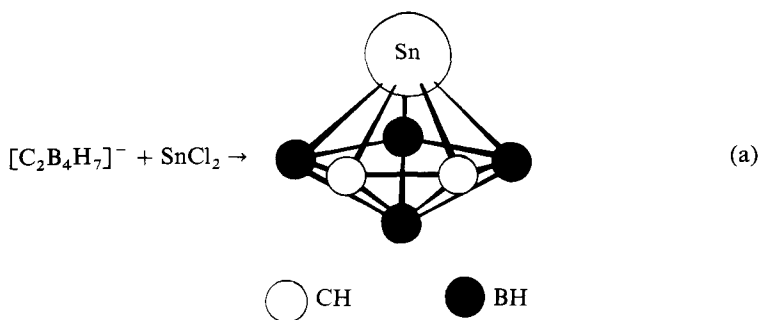


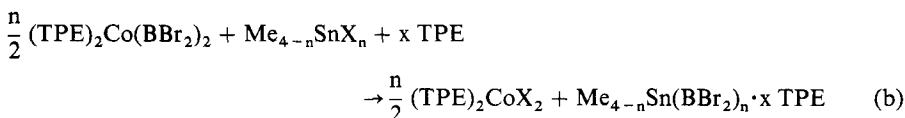
TABLE 1. TIN HALIDES WITH BORANE ANIONS

Borane anion	Tin halide	T (°C)	Time (h)	Product	Yield (%)	Ref.
$[\text{B}_5\text{H}_8]^-^a$	Me_3SnCl	−78 to −30	1	$\mu\text{-Me}_3\text{SnB}_5\text{H}_8$	60	2
$[\text{B}_{10}\text{H}_{13}]^-^b$	Me_3SnCl	75	$1\frac{1}{2}$	$\text{Me}_2\text{SnB}_{10}\text{H}_{12}$	18	3
$[\text{C}_2\text{B}_4\text{H}_7]^-^b$	Me_3SnBr	−196 to −23	1	$\mu\text{-Me}_3\text{SnC}_2\text{B}_4\text{H}_7$	66	5
$[\text{Me}_2\text{C}_2\text{B}_4\text{H}_5]^-^b$	SnCl_2	−196 to 23	1	$\text{SnMe}_2\text{C}_2\text{B}_4\text{H}_4$	4	6
$[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}^b$	SnCl_2	80	24	$\text{SnC}_2\text{B}_9\text{H}_{11}$	75	7
$[(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}]^-^b$	SnCl_2	−196 to 25	1	$\text{SnFe}(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2$	10	8

^a Lithium salt.

^b Sodium salt.

With uncomplexed TPE, the reaction can be extended to include $\text{Me}_{4-n}\text{Sn}(\text{BBr}_2)_n \cdot \text{TPE}$, unattainable in the uncomplexed state:



The TPE required varies with organotin halide, leading to values of $x = 3$ or 4 in the final products (see Table 1)

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5.3.17.3.2. with Boron Hydride Anions.

The scope for Sn—B bond formation is narrower than for Si (§5.7.3.2) and Ge (§5.3.12.3)¹. The reactions are complex, with Sn metal and free carborane accompanying the stannaborane as products, the latter thus being obtained in poor yield¹ (Table 1).

Lower boranes, e.g., $[\text{B}_5\text{H}_8]^-$, with Me_3SnCl give² $\mu\text{-Me}_3\text{SnB}_5\text{H}_8$, but higher boranes result in more complex reactions and concomitant low yields^{3,4}.

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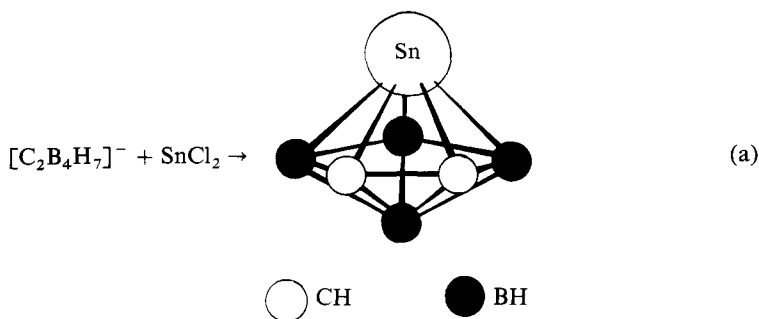


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$[\text{Me}_2\text{C}_2\text{B}_4\text{H}_5]^-$ ^b	SnCl_2	−196 to 23	1	$\text{SnMe}_2\text{C}_2\text{B}_4\text{H}_4$	4	6
$[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ ^b	SnCl_2	80	24	$\text{SnC}_2\text{B}_9\text{H}_{11}$	75	7
$[(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}]^-$ ^b	SnCl_2	−196 to 25	1	$\text{SnFe}(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2$	10	8

^a Lithium salt.

^b Sodium salt.

With $[\text{C}_2\text{B}_5\text{H}_7]^{2-}$, SnCl_2 produces only traces of stannacarboranes, Sn metal and $\text{C}_2\text{B}_5\text{H}_7$ being the major products⁶, but better yields (> 60%) result from $[\text{C-SiMe}_3, \text{C-(R)-C}_2\text{B}_4\text{H}_5]^-$ where R = Me, Me_3Si ^{7,8}.

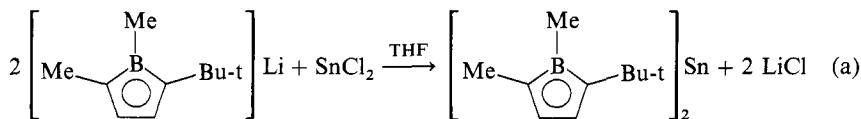
More complex carboranes, e.g., $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ and $[(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}]^-$, can also react. The former incorporates Sn(II) (from SnCl_2) into a closo-icosahedron⁹, whereas the latter forms a bimetallic carborane¹⁰, $\text{SnFe}(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2$, isostructural with its Ge analogue (see §5.3.12.3).

(K. C. MOLLOY)

1. R. N. Grimes, *Rev. Si, Ge Sn, Pb Compds.* 2, 223 (1977); a review of group-IVB carborane derivatives.
2. D. F. Gaines, T. V. Iorns, *J. Am. Chem. Soc.*, 90, 6617 (1968).
3. R. E. Loffredo, A. D. Norman, *J. Am. Chem. Soc.*, 93, 5587 (1971).
4. N. N. Greenwood, B. Youll, *J. Chem. Soc., Dalton Trans.*, 158 (1975).
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6. K-S. Wong, R. N. Grimes, *Inorg. Chem.*, 16, 2053 (1977).
7. N. S. Hosmane, N. N. Sirmokadam, R. H. Herber, *Organometallics*, 3, 1665 (1984).
8. N. S. Hosmane, P. De Meester, N. Madar, S. B. Potts, S. S. C. Chu, R. H. Herber, *Organometallics*, 772 (1986).
9. R. W. Rudolph, R. L. Voorhees, R. E. Cochoy, *J. Am. Chem. Soc.*, 92, 3351 (1970).
10. W. H. Maxwell, K-S. Wong, R. N. Grimes, *Inorg. Chem.*, 16, 3094 (1977).

5.3.17.3.3. with Boron Heterocycles.

The sandwich anion $[\text{h}^5\text{-C}_5\text{H}_5\text{CoC}_2\text{B}_2\text{C}]^-$ ($\text{C}_2\text{B}_2\text{C}$ is 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl) reacts with SnCl_2 to yield the tetra-decker $(\text{h}^5\text{-C}_5\text{H}_5\text{CoC}_2\text{B}_2\text{C})_2\text{Sn}$ in 69% yield¹. With 1-t-butyl-2,3-dimethyl-1H-2,3-dihydro-1,2-azaborolyl lithium a sandwich compound is formed in 49% yield²:



(K. C. MOLLOY)

1. H. Wadepohl, H. Pritzkow, W. Siebert, *Organometallics*, 2, 1899 (1983).
2. G. Schmid, D. Zaika, R. Böse, *Angew. Chem., Int. Ed. Engl.*, 24, 602 (1985).

5.3.17.4. Utilizing Stannylenes as Electron-Pair Donor Bases

Tin-boron bonds¹ are not formed in an electron-pair acceptor acid–electron-pair donor base interaction between $(\text{C}_5\text{H}_5)_2\text{Sn(II)}$ and BF_3 ², or using³ $[\text{SnCl}_3]^-$. Halogen transfer to yield fluoroborate anions $[\text{XBF}_3]^-$, X = F, Cl takes place instead^{2,4}. With $\text{Sn}(\text{NMe}_2)_2$ toward BF_3 , the complex products may involve lone pairs on both Sn and nitrogen⁵.

Definitive verification of an $\text{Sn} \rightarrow \text{B}$ bond via stannylenes lone-pair donation is still awaited⁶.

(K. C. MOLLOY)

1. P. G. Harrison, J. J. Zuckerman, *J. Am. Chem. Soc.*, 92, 2577 (1970).
2. T. S. Dory, C. L. Barnes, J. J. Zuckerman, *J. Organomet. Chem.*, 281, C1 (1985).

5.3. Formation of Bonds

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5.3.17. Formation of the Sn—Boron Bond

5.3.17.4. Utilizing Stannylenes as Electron-Pair Donor Bases

With $[\text{C}_2\text{B}_5\text{H}_7]^{2-}$, SnCl_2 produces only traces of stannacarboranes, Sn metal and $\text{C}_2\text{B}_5\text{H}_7$ being the major products⁶, but better yields ($> 60\%$) result from $[\text{C-SiMe}_3, \text{C-(R)-C}_2\text{B}_4\text{H}_5]^-$ where $\text{R} = \text{Me}, \text{Me}_3\text{Si}$ ^{7,8}.

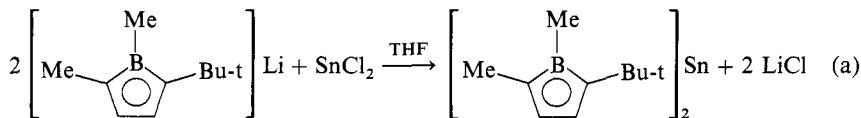
More complex carboranes, e.g., $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ and $[(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}]^-$, can also react. The former incorporates Sn(II) (from SnCl_2) into a closo-icosahedron⁹, whereas the latter forms a bimetallic carborane¹⁰, $\text{SnFe}(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)_2$, isostructural with its Ge analogue (see §5.3.12.3).

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5.3.17.3.3. with Boron Heterocycles.

The sandwich anion $[\text{h}^5\text{-C}_5\text{H}_5\text{CoC}_2\text{B}_2\text{C}]^-$ ($\text{C}_2\text{B}_2\text{C}$ is 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl) reacts with SnCl_2 to yield the tetra-decker $(\text{h}^5\text{-C}_5\text{H}_5\text{CoC}_2\text{B}_2\text{C})_2\text{Sn}$ in 69% yield¹. With 1-t-butyl-2,3-dimethyl-1H-2,3-dihydro-1,2-azaborolyl lithium a sandwich compound is formed in 49% yield²:



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Definitive verification of an $\text{Sn} \rightarrow \text{B}$ bond via stannylene lone-pair donation is still awaited⁶.

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5.3. Formation of Bonds

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5.3.17. Formation of the Sn—Boron Bond

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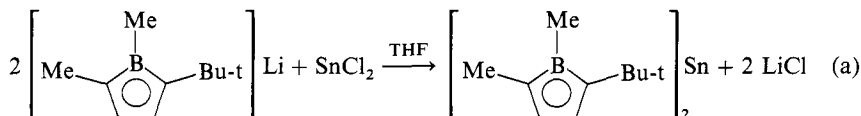
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5.3.18. Formation of the Sn—Al Bond

5.3.18.1. from the Elements

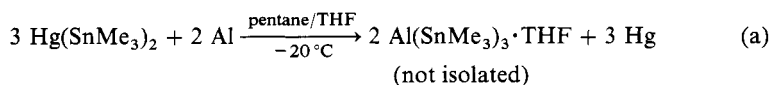
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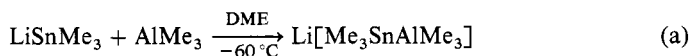
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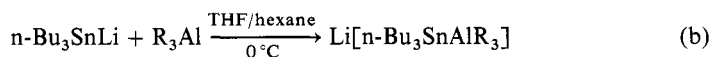
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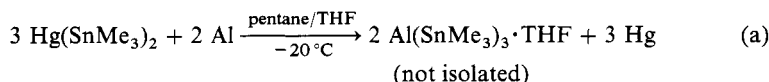
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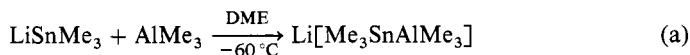
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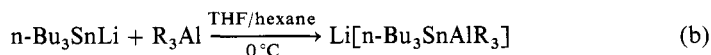
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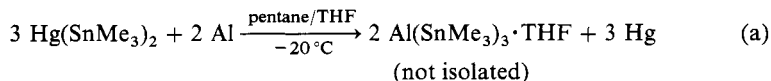
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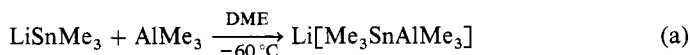
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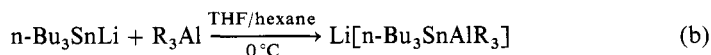
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Organostannyl aluminum reagents can be prepared by R_3SnLi with R_3Al or $\text{R}_2\text{AlCl}^{3-6}$:



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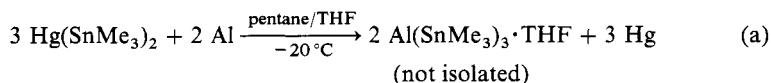
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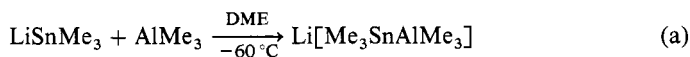
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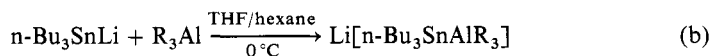
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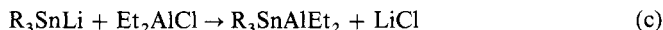


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where R = Me, Et, or:



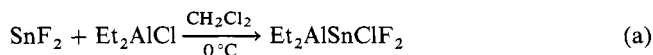
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5.3.18.4. from Sn(II) Halides with Al Alkyls

Reaction of SnF₂ with Et₂AlCl yields Et₂AlSnClI₂:



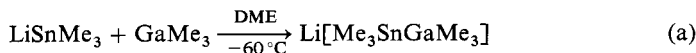
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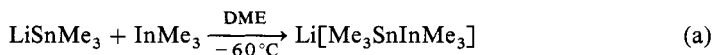


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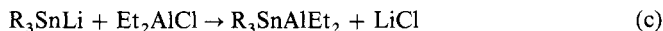
5.3. Formation of Bonds

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5.3.18. Formation of the Sn—Al Bond

5.3.18.4. from Sn(II) Halides with Al Alkyls

where R = Me, Et, or:



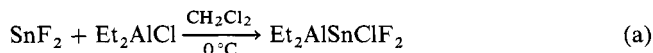
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6. S. Matsubara, T. Nonaka, Y. Okuda, S. Kanemoto, K. Oshima, H. Nozaki, *Bull. Chem. Soc. Jpn.*, **58**, 1480 (1985).

5.3.18.4. from Sn(II) Halides with Al Alkyls

Reaction of SnF_2 with Et_2AlCl yields $\text{Et}_2\text{AlSnClF}_2$:



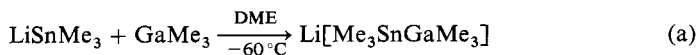
The compound was not isolated, but the solution taken for use in situ¹.

(L. RÖSCH)

1. S. Matsubara, K. Wakamatsu, Y. Morizawa, N. Tsuboniwa, K. Oshima, H. Nozaki, *Bull. Chem. Soc. Jpn.*, **58**, 1196 (1985).

5.3.19. Formation of the Sn—Ga Bond

The formation of a compound with a Sn—Ga bond in 1,2-dimethoxyethane (DME) is established by NMR^{1,2}:



(L. RÖSCH)

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2. A. T. Weibel, J. P. Oliver, *J. Organomet. Chem.*, **74**, 155 (1974).

5.3.20. Formation of the Sn—In Bond

The formation of a compound with a Sn—In bond in 1,2-dimethoxyethane (DME) is established by NMR^{1,2}:



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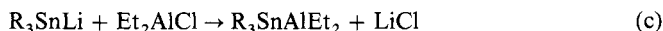
5.3. Formation of Bonds

233

5.3.18. Formation of the Sn—Al Bond

5.3.18.4. from Sn(II) Halides with Al Alkyls

where R = Me, Et, or:



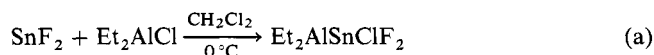
where R = Me, n-Bu. These compounds are not isolated, but the solutions used in situ³⁻⁶.

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Reaction of SnF_2 with Et_2AlCl yields $\text{Et}_2\text{AlSnClI}_2$:



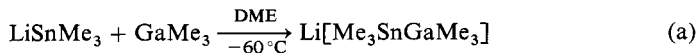
The compound was not isolated, but the solution taken for use in situ¹.

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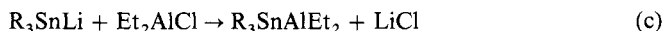
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233

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5.3.18.4. from Sn(II) Halides with Al Alkyls

where R = Me, Et, or:



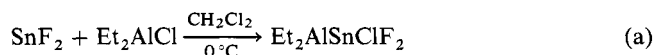
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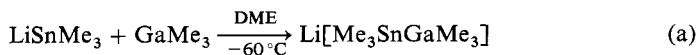
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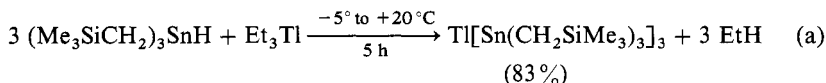
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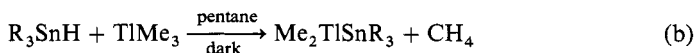
5.3.21. The Formation of the Sn—Tl Bond

5.3.21.1. from Organotin Hydrides with Organothalliums

A stable organotin–Tl compound is obtained¹:



Other compounds, unstable at RT, are prepared from TlMe_3 with Ph_3SnH or Et_3SnH in pentane at low T^2 :



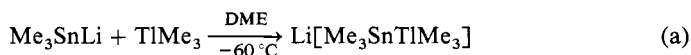
where if $\text{R} = \text{Ph}$ and $T = -10^\circ$ to -5°C , the yield is 65%, and if $\text{R} = \text{Et}$ and $T = -30^\circ$ to -20°C , 65%. Attempts to prepare $\text{Tl}(\text{SnEt}_3)_3$ from Et_3SnH with $\text{Tl}(\text{GeEt}_3)_3$ or TlEt_3 fail, and only decomposition products can be isolated³.

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1. G. S. Kalinina, E. A. Shchupak, N. V. Vyazankin, G. A. Razuvaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1342 (1976).
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5.3.21.2. from Stannyl–Alkali-Metal Reagents with Tl Alkyls

Addition of TlMe_3 to LiSnMe_3 in 1,2-dimethoxyethane (DME) at -60°C leads to the formation of several products, three of which contain Sn—Tl bonds as indicated by NMR. One of the main products is $\text{Li}[\text{Me}_3\text{SnTlMe}_3]$:

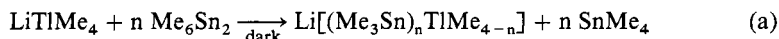


(L. RÖSCH)

1. A. T. Weibel, J. P. Oliver, *J. Am. Chem. Soc.*, 94, 8590 (1972).

5.3.21.3. from Organodistannanes with Li Tetramethylthallate

The cleavage of Me_6Sn_2 with LiTlMe_4 in 1,2-dimethoxyethane (DME) at RT leads, according to the stoichiometry, to products with Sn—Tl bonds:



The composition of $\text{Li}[\text{Me}_3\text{SnTlMe}_3]$, $\text{Li}[\text{Me}_3\text{Sn}_2\text{TlMe}_2]$, $\text{Li}[(\text{Me}_3\text{Sn})_3\text{TlMe}]$ and $\text{Li}[(\text{SnMe}_3)_4\text{Tl}]$ obtained in this way is established by NMR of the solutions. The compounds are not isolated¹.

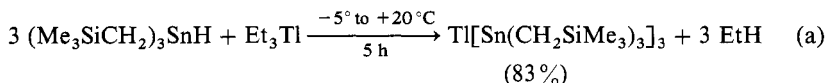
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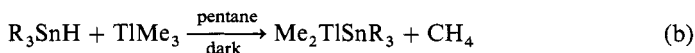
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5.3.21.1. from Organotin Hydrides with Organothalliums

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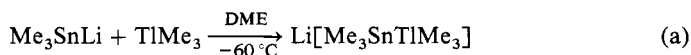
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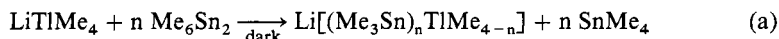


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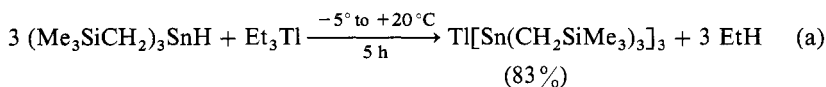
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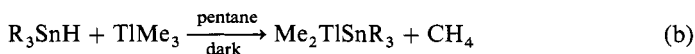
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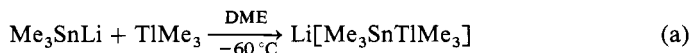
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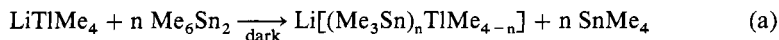


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5.3. Formation of Bonds

235

5.3.22. Formation of the Pb—Boron Bond

5.3.22.3. from Lead Halides

5.3.22. Formation of the Pb—Boron Bond**5.3.22.1. from the Elements**

Only scant evidence of lead boride formation¹ exists. Borides of lead are unlikely in view of the high second ionization potential of Pb².

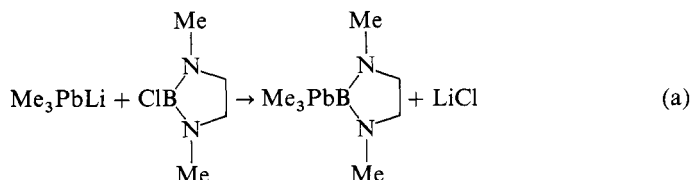
(K. C. MOLLOY)

1. J. Cueilleron, P. Pichat, Fr. Pat. 1,471,238 (1967); *Chem. Abstr.*, 67, 74,972 (1967).

2. R. Thompson, *Prog. Boron Chem.*, 2, 177 (1970).

5.3.22.2. from Plumbyl-Alkali-Metal Reagents with Haloaminoboranes

By analogy to Si (see §5.3.7.4.1), Ge (see §5.3.12.2.1) and Sn (see §5.3.17.2.2), trimethylplumbyllithium reacts at -78°C to displace Cl^- from haloaminoboranes and form a Pb—boron bond:



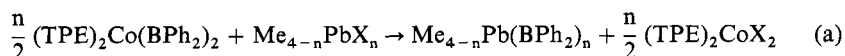
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Organoboron-Co compounds are precursors to metal-boron bonds as established for Sn (see §5.3.17.3.1) and provide a RT route to otherwise inaccessible organoboron-Pb compounds¹:



where $\text{TPE} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. No experimental details are available².

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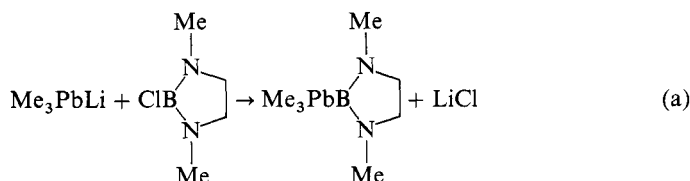
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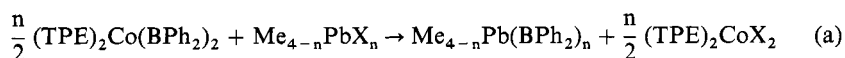
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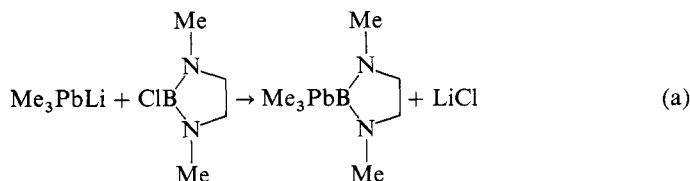
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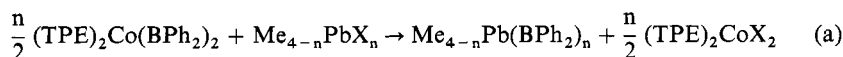
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1. G. Schmid, *Angew. Chem., Int. Ed. Engl.*, 9, 819 (1970).
2. H. Schafer, Diss., Univ. Marburg, 1969; quoted in ref. 1.

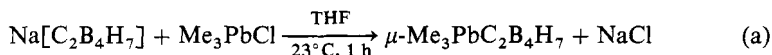
5.3. Formation of Bonds

5.3.22. Formation of the Pb—Boron Bond

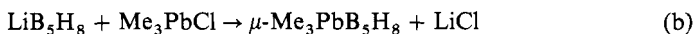
5.3.22.4. from Lead(II) Acetate and Carborane Anions

5.3.22.3.2. with Borane and Carborane Anions.

The low thermal stability of boron-plumbylated boranes and carboranes limits this route to Pb—boron bonds. Trimethyllead, however, can be inserted into the $[C_2B_4H_7]^-$ carborane cage in tetrahydrofuran (THF) in 70% yield¹:



Similarly, at low-T the borane anion $[B_5H_8]^-$ also yields a plumbyl-bridged cluster, although the product is thermally unstable at RT²:



Small carboranes, such as $NaC_2B_4H_7$ and its C,C-dimethyl derivative, also react with $PbBr_2$ to insert Pb(II) into the cage to generate *closo*- $PbC_2B_4H_6$ or *closo*- $PbMe_2C_2B_4H_4$, but in both cases only low yields of thermally unstable compounds are achieved³.

With $[closo-C_2B_5H_7]^{2-}$ and $[Me_2C_2B_4H_4]_2FeH]^-$, $PbBr_2$ does not yield isolable metallacarboranes^{3,4}.

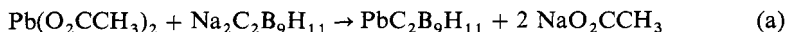
(K. C. MOLLOY)

1. A. Tabereaux, R. N. Grimes, *Inorg. Chem.*, **12**, 792 (1973).
2. D. F. Gaines, T. V. Iorns, *J. Am. Chem. Soc.*, **90**, 6617 (1968).
3. K-S. Wong, R. N. Grimes, *Inorg. Chem.*, **16**, 2053 (1977).
4. W. M. Maxwell, K-S. Wong, R. N. Grimes, *Inorg. Chem.*, **16**, 3094 (1977).

5.3.22.4. from Lead(II) Acetate and Carborane Anions

Lead(II) acetate can be used as an alternative to lead(II) halides with carborane anions, offering advantages in solubility in certain systems.

With $Na_2C_2B_9H_{11}$, a *closo*-, icosahedral carborane with apical Pb(II) is produced in 36% yield¹:



(K. C. MOLLOY)

1. R. W. Rudolph, R. L. Voorhees, R. E. Cochoy, *J. Am. Chem. Soc.*, **92**, 3351 (1970).

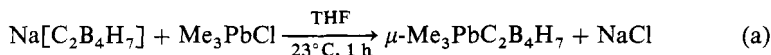
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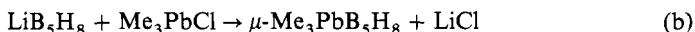
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With $[closo-C_2B_5H_7]^{2-}$ and $[Me_2C_2B_4H_4)_2FeH]^-$, $PbBr_2$ does not yield isolable metallocarboranes^{3,4}.

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5.4. Formation of Bonds between Elements of Group IVB(C, Si, Ge, Sn, Pb) and Group IIA (Be, Mg, Ca, Sr, Ba, Ra)

5.4.1. Introduction

Because of the overriding historical and practical importance of the organomagnesium and organomagnesiumhalide reagents, the chemistry of the chemistry of the carbon—magnesium compounds has been gathered together. Combinations involving the other group-IIA elements with the lower congeners of group IVB are more rare with some not as yet known. Their treatment completes Volume 10.

(J. J. ZUCKERMAN, ED.)

5.4.2. Formation of the Carbon—Mg Bond

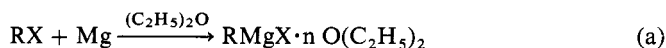
5.4.2.1. from the Elements

This topic is dealt with in §5.10.2.

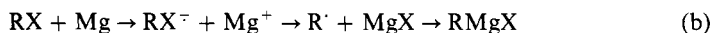
5.4.2.2. from Mg Metal and its Alloys

5.4.2.2.1. by Action of Organic Halides or Other Derivatives on the Metal.

Organomagnesiums are synthetic tools in organic and organometallic chemistry since the discovery that organomagnesium halides can be prepared from an organic halide with Mg metal in a basic, aprotic solvent¹, such as Et₂O:



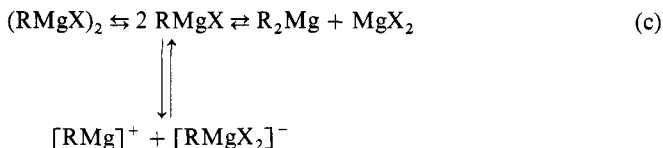
This reaction is of simple stoichiometry and often occurs with great ease and in high yield. Nevertheless, its mechanism is complex and difficult to unravel. It involves radical intermediates²⁻⁵ and occurs with a mass-transfer-limited rate⁶:



↓
side products

The organomagnesium-halide reagents are sensitive to air and moisture and are, therefore, used directly in solution for further transformations. However, they may be isolated as white, frequently **self-igniting solids** that are stable to ca. 100°–150°C. Their structures in the solid state involve coordination numbers for Mg varying from three to six², but the majority of cases show Mg to be tetracoordinated, with one organic group,

one halogen and two ethers (or *t*-amines) as ligands³. Unless of direct relevance for the reaction to be studied, the coordinated solvent molecules usually are not written, although they form an integral part of the reagent and are important for the structure and reactivity. In solution, the structure of the reagents can be complex owing to association and disproportionation equilibria and, to a minor extent, to dissociation^{2,9,10}, which are influenced by R, X, the solvent, the concentration and T:



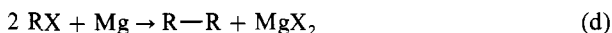
Ethylmagnesium bromide, e.g., exists predominantly as such in Et₂O¹¹, whereas in tetrahydrofuran (THF) disproportionation becomes prominent¹².

Organomagnesium chemistry receives vast attention. It is, therefore, impossible to deal with it concisely. Reviews facilitate entrance into this field^{2,9,10,13-17}.

(i) General Procedure. Because of the sensitivity of organomagnesiums toward O₂ and air, reactions are conducted in dry apparatus under an inert gas, particularly if the scale is small. Nitrogen (of high purity, otherwise purification by removal of O₂ and H₂O is required¹⁸) or, preferably, Ar is used for this purpose. If high standards are required, e.g., for structural investigations, all manipulations should be performed in a high-vacuum system¹⁹. Similarly, the reagents and solvents should be of high quality; special requirements are treated below.

A normal reagent, e.g., from an alkyl bromide with Mg metal in Et₂O or THF, is prepared as follows. A three-necked flask equipped with inert gas inlet, mechanical or magnetic stirring, a reflux condenser, a dropping funnel and, if desired, an internal thermometer, and containing 1 equiv or xs (normally 5–10%) of Mg metal is heated by a flame under a stream of inert gas to remove air and moisture. After cooling, a small amount of the organic halide (ca. 0.01 equiv) in a few mL of dry solvent is added. After an induction period of usually 1–15 min, the reaction starts. It can be recognized by evolution of heat, boiling and formation of a milky suspension, which suddenly clears up. This phase of the reaction may give trouble, and special procedures are mentioned in §5.4.2.2.1(iii). Next, the rest of the halide (0.5–1.5M) is added slowly at a rate such that the mixture keeps boiling gently, and the reaction does not stop. Slow addition, in particular with reactive halides, reduces the formation of byproducts. Toward the end, heating to reflux for at least 15–60 min is required.

The formation of the reagent can be checked by qualitative color tests²⁰ or by titration. For this purpose the volume of the solution should be measured or estimated as accurately as possible. An aliquot is taken, cautiously hydrolyzed and titrated with HCl against methyl-red indicator. If desired, this may be followed by a titration of total Mg with complexon (ethylenediaminetetraacetic acid)²¹; the difference between total and basic Mg is a measure for the xs MgBr₂ formed in, e.g., radical side reactions. The radicals lead to radical coupling products, R—R, but they may also disproportionate, attack the solvent or rearrange:



For most purposes these titrations furnish sufficient information. In certain cases, it may be also desirable to determine the amount of active C—Mg bond present directly; several procedures for doing so are reviewed¹⁷.

The general procedure above must be modified for certain organic halides. These special procedures are treated in §5.4.2.2.1(iv).

(ii) **The Solvent.** Alkyl halides do react with Mg metal, in the form of codeposited atoms at low T^{22-24} (see §5.8.2.3.2, 5.8.2.4.6, 5.8.2.5.3, 5.8.2.6.5, 5.8.2.7.6, 5.8.2.9.3, 5.8.2.9.5 and 5.8.2.16.4), or as a film obtained by vacuum sublimation^{25,26}; Mg turnings react at 80° – 150°C^{27} . The yields are low, and side reactions are dominant. Therefore, the reaction is nearly always performed in a solvent.

As mentioned in §5.4.2.2.1(i) the purity of the reagents may be critical for success; this also holds for the solvent employed. Ethers should be free of peroxides (washing with aq FeSO_4). They are dried by refluxing and distillation from Na wire or Na-K alloy under an inert atmosphere. Absence of O_2 and H_2O can be achieved by distillation from Na metal and benzophenone (blue benzophenone-ketyl, or better the copper-colored disodium adduct), from LiAlH_4 or from organomagnesium-halide reagents, such as $\text{C}_2\text{H}_5\text{MgBr}$.

On a laboratory scale, the reaction is commonly and conveniently conducted in an aprotic, electron-pair donor base solvent, which not only serves to complex and dissolve the organomagnesium-halide reagent, thereby removing the reaction product from the metal surface, but also plays an essential, beneficial role in the intermediate stages⁴. Diethyl ether and THF are usually the solvents of choice. Dimethyl ether is superior, but because of its low bp (-23°C) it is seldom used. Other ethers occasionally used are 1,4-dioxane, 1,2-dimethoxyethane (DME), diisopropyl ether²⁸, furan and 3,4-dihydro-2H-pyran, formals²⁹ and acetals³⁰. Vinyl and aryl ethers are less suitable because of their reduced basicity; also, cleavage reactions may occur. Similarly, sterically hindered ethers are not sufficiently basic. Some of these ethers give sluggish and incomplete reactions because of precipitates that deactivate the Mg surface; benzene, toluene, xylenes or naphthalene as co-solvents often can prevent the formation of such precipitates. Tertiary amines, such as Et_3N , are seldom used. Highly polar aprotic solvents are hexamethylphosphortriamide (HMPA)³¹, although it is of limited stability, and recently tetraethylsulfamide is suggested as a stable polar solvent for the preparation and use of organomagnesium-halide reagents³².

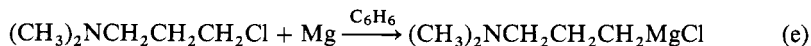
Different ethers have specific advantages or disadvantages in combination with organic halides, depending on the structure of the latter. These are discussed in §5.4.2.2.1(iv).

It may be desirable to avoid ethers despite their valuable properties. **Ethers are sometimes toxic** (e.g., THF³³, but also HMPA³⁴) and less attractive industrially because of their **high inflammability and the hazards of peroxide formation**. Ethers are also more expensive than, e.g., hydrocarbons. Consequently, considerable effort is invested in the preparation of the reagents in hydrocarbons and other nonethereal solvents.

In pure hydrocarbons the formation reaction needs elevated T (80 – 150°C) and the organomagnesiums thus obtained have properties different from those of the normal, solvated species³⁵: they are less selective, can be used as cocatalysts in Al/Ti-type polymerizations and have a low halogen (X) content; a disadvantage is their insolubility, so that slurries are obtained that are difficult to handle. Higher alkyl halides, in particular alkyl iodides, give soluble products and good results³⁶. In some cases, xs organic halides may be used instead of hydrocarbons, e.g., in the preparation of phenylmagnesium chloride³⁷ or in a continuous process for the manufacture of cyclohexylmagnesium chloride³⁸.

If the reactions of organic halides and Mg metal are performed in hydrocarbons with the addition of 1 or a few equiv of an electron-pair donor base, they occur much more

readily; yields, solubility and further transformations are improved without losing the advantage of an essentially hydrocarbon medium, and THF³⁹, Et₃N and HMPA⁴⁰ are used for this purpose. Addition of other oxygen-containing species, such as mixed alkoxides {Mg(OCH₂CH₂OCH₂CH₂OCH₃)OCH₃ or Na[AlH₂(OCH₂CH₂OCH₃)₂]}, promotes the reaction⁴². If the organic halides contain electron-pair donor base groups in the molecule, the addition of external base is not necessary, e.g.⁴⁴:



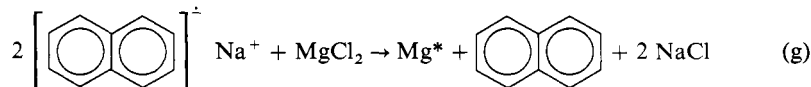
(iii) **The Metal.** For most preparative purposes, commercially available Mg turnings of good quality are satisfactory. Their content of transition-metal impurities is low and does not interfere with the formation and the transformation of the organomagnesiums. However, larger amounts of impurities both impair the yield of the reagents and influence the course of their further reactions⁴⁵.

If difficulties are encountered in the preparation of special organomagnesium-halide reagents, it may be useful to employ Mg metal of higher purity. Purification can be achieved by (double or triple) sublimation in a steel apparatus, or by zone melting. Sublimation in a glass vessel also gives a reactive Mg mirror, but at the required T the Mg metal attacks the glass wall^{25,26}. With triply sublimed Mg metal and other high-purity reagents in a high-vacuum system, the usually encountered induction period is reduced to zero.

Several forms of highly reactive Mg metal are available; they permit reaction with organic halides that otherwise could not react. Finely divided and highly reactive black Mg powder is prepared by the reduction of anhydr MgCl₂ with potassium metal in refluxing THF^{46,47}. This powder forms a reagent even at -78°C or with aryl fluorides, which are otherwise unreactive:



A similarly reactive Mg powder is formed from the Na naphthalene radical-anion⁴⁸:



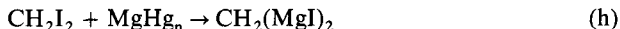
The formation of organomagnesium species by cocondensation of Mg atoms with organic halides was mentioned in §5.4.2.2.1(i)^{22,24}. A highly reactive Mg slurry is obtained by cocondensation of Mg vapor with solvents such as THF or hexane. By partial warming, clustering occurs to give a finely divided metal that reacts at low T or with unreactive halides⁴⁹. A highly reactive form of the metal is available as an Mg-anthracene adduct⁵⁰.

In less tenacious cases, more conventional and simpler methods of activating Mg metal may be applied. Nearly all achieve their goal ultimately by increasing the activity of the Mg surface (number of active spots or lattice irregularities; cleaning the surface of inhibitors, such as oxides, or reaction products). They may be divided into two categories: mechanical and chemical activation.

Mechanical activation may be achieved by scratching or scraping the metal, either before the reaction or continuously while the reaction is going on. In the simplest case, stirring commercial Mg turnings for 24 h under N₂ achieves activation in the preparation of 4-dimethylaminophenylmagnesium bromide⁵¹. Enhancement and activation of the surface area by grinding or filing has an accelerating effect, as does high-speed stirring⁵²

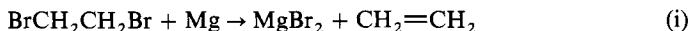
or ultrasound treatment⁴⁷ during the reaction. The highly activated, finely dispersed metal preparations mentioned above⁴⁶⁻⁴⁹ are an extreme form of mechanical activation.

Chemical activation is applied more widely. The oldest⁵⁴ but still a useful method⁵⁵ consists of heating Mg turnings with I₂ prior to reaction. Alloys of Mg, e.g. with Cu⁵⁵ are recommended, but their usefulness is doubtful, particularly because they may decrease the yield of reagent and the course of the ensuing transformations. Amalgamation of the Mg with HgCl₂ is occasionally applied, and in special cases Mg amalgam (containing 1-3 % Hg) is superior to pure Mg, e.g.^{28,56}:



Reactive halides, e.g., methyl iodide, ethyl bromide or 1,2-dibromoethane, help to overcome the induction period. Many other activating additions are of doubtful or limited value⁵⁷.

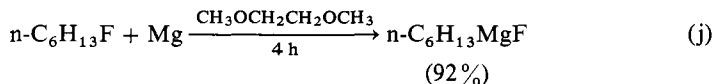
The entrainment method cannot be distinguished from the application of this last group of initial activators. This approach is applied when the organic halide is exceptionally difficult to react with Mg metal. An active halide, e.g., EtBr or dibromoethane, is added continuously to the metal together with the halide of which the reagent is to be formed. A disadvantage of this method is the simultaneous formation of the entrainer reagent, except for 1,2-dibromoethane, which gives MgBr₂ and ethylene as noninterfering side products:



(iv) **The Organic Halide.** Both the halogen and the organic portion of the starting material influence the reaction, as does the solvent. It is important to choose the proper combination of these three variables; otherwise the reaction may be too sluggish (e.g., organic chlorides in hydrocarbons, sometimes in ethers) or incomplete. Likewise, the reaction may be too fast (e.g., benzyl halides in THF), leading predominantly to undesired side reactions, or other complications may arise (e.g., with alkyl iodides in THF).

(a) **The Halogen.** The order of reactivity of organic halides in the reaction is: F ≪ Cl < Br < I.

Organic fluorides do not normally react with Mg metal. After earlier failures, a successful preparation⁵⁸ using THF or DME and catalysts, of which I₂ proves to be the best, yields, e.g.:



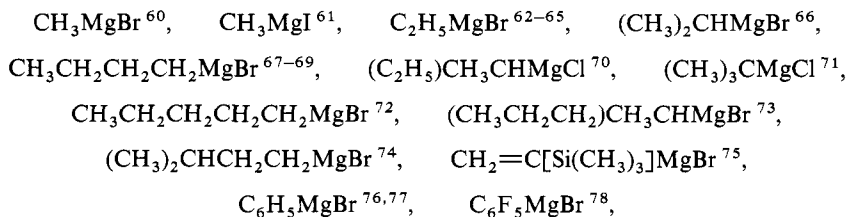
Fluorobenzene reacts only with highly reactive Mg metal⁴⁶. Although other methods for organomagnesium fluorides are available (see §5.4.2.5), they are of limited practical value.

Organic chlorides, bromides and iodides react with increasing ease in that order. Each has certain advantages and disadvantages. Organic chlorides are cheap and produce reagents in high yield and with few side products, but their reactivity is low, so that strongly basic solvents are often required or the reaction time must be long. Furthermore, organomagnesium chlorides tend to associate^{9,10} and to be poorly soluble in, e.g., Et₂O. Organic bromides balance advantages and disadvantages in the most acceptable way and are, therefore, the most convenient halides. Diethyl ether is a good solvent; in THF both the ease of reaction and the yields are even better. Organic iodides are the easiest and fastest to react with Mg metal. However, side reactions, such as radical

processes during the formation or coupling between organomagnesium iodide and unreacted organic iodide, may become prominent. Particularly in THF, alkyl iodides give poor results; slurries are formed that have a high MgI_2 content⁵⁹; methylmagnesium iodide cannot be prepared directly in THF. Weaker basic solvents, such as Et_2O , give better results.

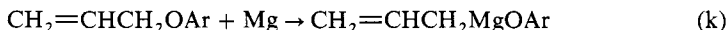
The description of the behavior of organic halides (see above) holds only for ordinary alkyl or aryl halides. As mentioned earlier, the organic portion of the starting material can have a decisive influence on the reactivity [see §5.4.2.1.(iv)(b)].

Satisfactory preparations of alkyl- and arylmagnesium halides are described:

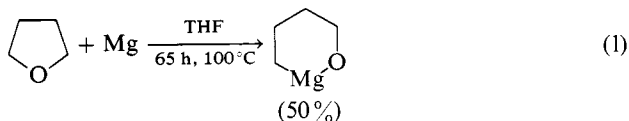


2,4,6-trimethylphenylmagnesium bromide^{79,80}, 1-naphthylmagnesium bromide^{81,82} and 9-phenanthrylmagnesium bromide⁸³. Others are mentioned in §5.4.3.2.1(iv) (b).

Other groups can take over the role of the halogen. Organomagnesiums can be prepared from alkyl sulfates⁸⁴. In allyl ethers⁸⁴ an aryloxy group can act as a pseudohalogen (Ar = phenyl, α -, or β -naphthyl) to form allylmagnesium reagents in good yields:

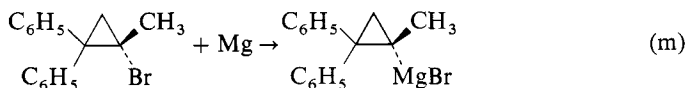


The allyl group may be substituted by phenyl but not by methyl groups. An organomagnesium reagent can be prepared by cleaving an unactivated ether bond with highly activated Mg metal⁸⁶:



(b) The Organic Portion. Ordinary primary and secondary alkyl and aryl bromides usually can be employed without problems in Et_2O . For the corresponding chlorides, the more strongly basic THF is mostly required; THF is less suited for alkyl iodides⁵⁹.

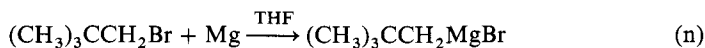
Optically active alkyl halides furnish optically active organomagnesium-halide reagents only when the metal is not bound to the asymmetrical carbon atom. An exception is (+)-(S)-1-methyl-2,2-diphenylcyclopropylmagnesium bromide³; although losing part of the original optical purity of the starting bromide in the formation reaction, the resulting organomagnesium-halide reagent is optically stable in solution once it is formed:



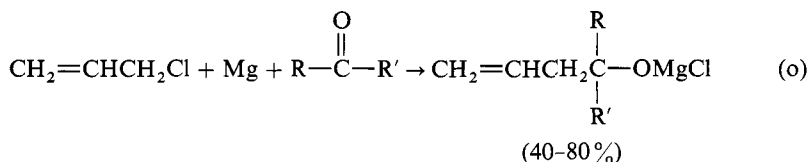
All other asymmetrical organomagnesium reagents lose their optical integrity in radical processes during formation³⁻⁶ or by exchange in solution⁸⁷.

Tertiary alkyl halides react with greater difficulty than their primary and secondary analogues. The bromides and iodides tend to eliminate halogen halide, but the chlorides can be converted to the organomagnesium-halide reagents^{71,88}. Cyclic secondary and tertiary halides resemble their acyclic analogues; for medium-sized rings, especially for cyclononylmagnesium bromide, lower yields are found (in Et₂O)⁸⁹.

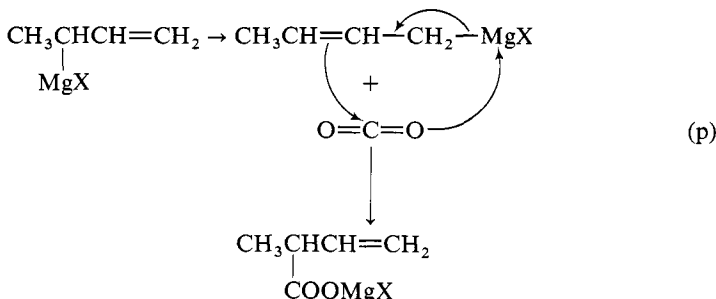
Some primary and other alkyl halides with special structural features pose problems. With increasing chain length ease of reaction decreases⁹⁰. Neopentyl chloride is difficult to transform to its organomagnesium-halide reagent, even in THF^{91,92}. The best method for the neopentyl reagent is from the bromide in THF⁹³:



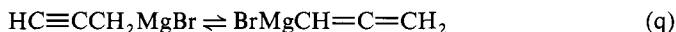
Allyl and benzyl halides are reactive, but often the yield of organomagnesiums is low, dimerization of the organic portion being the main reaction. For this reason, allyl halides frequently are used simultaneously with Mg metal and the substrate with which the intermediate organomagnesium species is to react^{94,95}:



Satisfactory methods are available, however, for the preparation of both allylmagnesium chloride in Et₂O⁹⁶ or THF⁹⁷ and allylmagnesium bromide in Et₂O⁹⁸. The allylmagnesiums undergo allylic rearrangement. For instance, 2-buten-1-ylmagnesium halides predominate in the equilibrium with their 1-buten-3-ylmagnesium isomers⁹⁹; however, in the reaction with most substrates, it is the latter structure that is incorporated into the product. This is explained by a cyclic¹⁰⁰ S_E2'-type transition state¹⁰¹, e.g., preparation^{103–105} of:

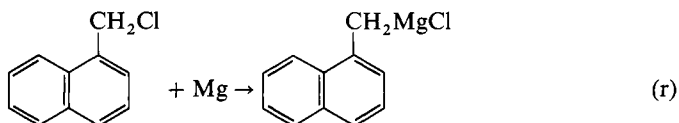


Propargylmagnesium halides are in equilibrium with their allenyl isomers¹⁰⁶ and react, depending on substitution pattern and the conditions, from one or both of the isomeric structures¹⁰⁷:



Benzyl halides also form dimers in a coupling side reaction; high dilution of benzyl chloride, however, leads to high yields of the organomagnesium-halide reagent¹⁰⁸. Depending on the substitution, other benzyl halides give more or less dimerization; e.g.,

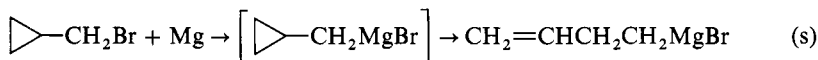
1-chloromagnesiomethylnaphthalene can be obtained in 90% yield under standard conditions¹⁰⁹:



Like allyl- and propargylmagnesium compounds, benzylmagnesium halides when reacted with a substrate give rise in part to products substituted at the allylic, i.e., here at the ortho position; THF favors reaction at the benzylic position¹¹⁰.

Many (cyclo)alkyl halides react with Mg metal but do not form organomagnesium-halide reagents with the original carbon skeleton, giving rise instead to rearranged products. This holds in particular for halides containing small rings or double bonds. Examples illustrate the types of rearrangements encountered.

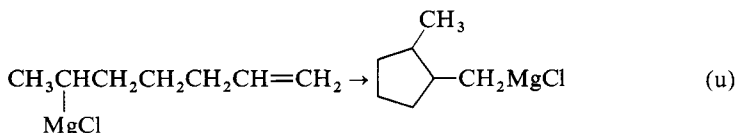
Cyclopropylmethylbromide in Et₂O reacts at RT to form 3-butenylmagnesium bromide¹¹¹; only at low T or by direct interception in the presence of an electrophile (e.g., H⁺ or CO₂) can the intermediate existence of cyclopropylmethylmagnesium bromide be demonstrated¹¹²:



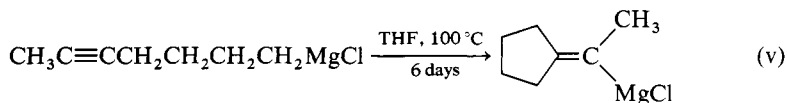
Cyclobutylmethyl chloride similarly leads to the rearranged product:



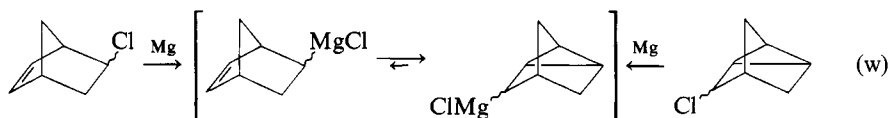
With larger rings, however, the ring-closed products are the more stable ones, so that the reverse reaction occurs, although under more drastic conditions, such as in boiling THF¹¹⁴:



Even triple bonds undergo this cyclization, under still more drastic conditions¹¹⁵:

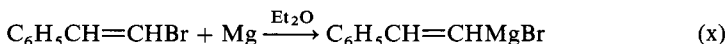


Similar rearrangements are observed in strained and bicyclic systems. The position of the equilibria may be reversed, e.g., in favor of the cyclopropylmethyl unit in nortricyclene¹¹⁶:

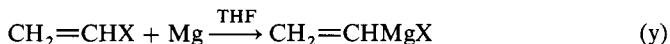


Unsaturated organomagnesium-halide reagents with Mg directly attached to an olefinic carbon—a substituted vinylmagnesium halide—are formed less easily than their

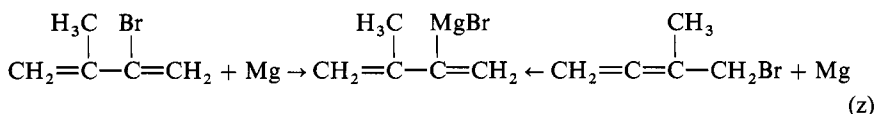
alkyl or aryl analogues. Although some substituted vinyl halides, such as β -bromostyrene, do react in Et_2O ¹¹⁷:



vinylmagnesium bromide itself and its alkyl-substituted derivatives are available only from THF^{118–120}:

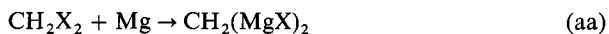


Cyclic vinylmagnesium halides react similarly, but in lower yield¹²¹. Isomerism around the double bond (E–Z) may be partly lost in the formation of the reagent; once formed, they are configurationally stable. Occasionally, rearrangements are encountered in polyunsaturated systems, e.g.^{122–124}:



Bifunctional organomagnesium-halide reagents are investigated both for their inherent structural interest and as synthons for other organometallic or organic compounds. The smaller representatives are not easily available from the corresponding halides, because side reactions usually prevail; their formation and chemistry are poorly known.

Surprisingly, dibromomethane and diiodomethane react with Mg metal or Mg amalgam in benzene–ether mixtures to form the bis-magnesium-halide reagent in 30–80% yield¹²⁵; diisopropyl ether raises the yield to 80–90%²⁸.

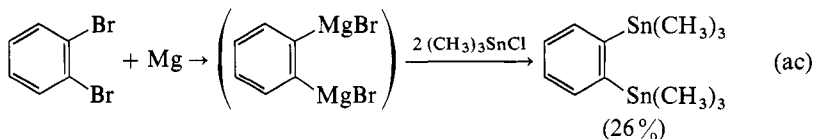


1,2-Bis-magnesium-halide reagents are difficult to prepare. 1,2-Dihaloalkanes react readily with Mg metal; this is the reason for the usefulness of 1,2-dibromoethane as an entrainment reagent [see §5.4.2.1(iii)]. However, the intermediate step of an α -halomagnesium- β -halo-substituted species occurs; as is discussed below, such species tend to eliminate Mg salts and form alkenes. Alkenes are the products actually observed:

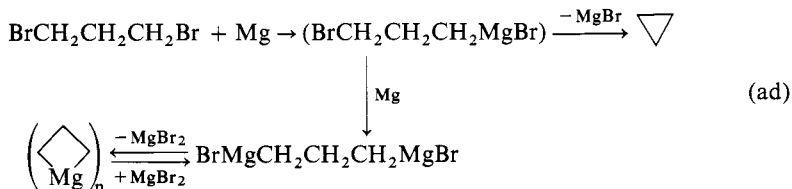


An exception is 1,2-dibromocyclopropane, which can be converted to the bis-magnesium halide reagent in ca. 15% yield^{126,127}; obviously, the strain involved in the alkene, cyclopropene, retards elimination of the intermediate monomagnesium halide reagent here.

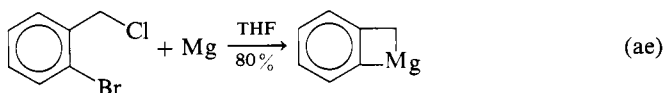
1,2-Dihalobenzenes give monomagnesium halide reagents that are often unstable and eliminate Mg halide and form benzyne¹²⁸. In a few cases 1,2-bis-magnesium halide reagents are obtained, e.g., from 3,4-dibromotoluene¹²⁹, 1,2-diiodobenzene¹³⁰ and 1,2-dibromobenzene¹³¹; here also the ring strain of benzyne retards the otherwise predominant elimination, e.g.:



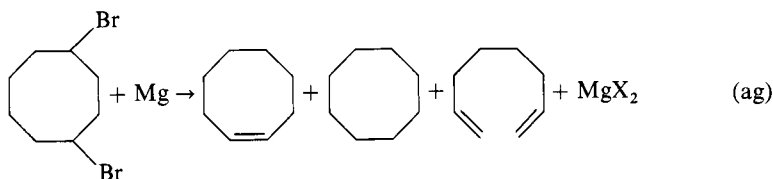
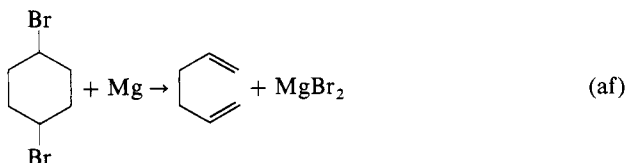
1,3-Bis(bromomagnesio)propane is prepared indirectly from the corresponding Hg derivative¹³². Again, the direct reaction of 1,3-dibromopropane gives complex side reactions of which the formation of cyclopropane is the major one¹³³:



The synthetically useful bis-magnesium-halide reagent can be prepared in ca. 30% yield under controlled conditions. It can be separated from all accompanying impurities by precipitation of the corresponding dialkylmagnesium (an oligomer of magnesacyclobutane). Addition of MgBr_2 in Et_2O reconstitutes and dissolves the bis-magnesium-halide reagent¹³⁴. Another useful 1,3-dimagnesium reagent is obtained as follows¹³⁵:



Organic dihalides, aliphatic or aromatic, with ≥ 4 carbon atoms between the two halogens do not present any difficulties other than those encountered with their monohalo analogues. To prevent coupling, which in this case may be favored by intramolecular ring closure, the addition of the dihalide should be slow; Et_2O is used^{136,137} but THF is preferable¹³⁸. With several cyclic dihalides, elimination or fragmentation occurs, e.g.^{139,140}:



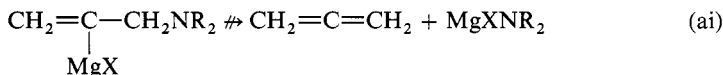
(v) **Functionally Substituted Reagents.** Some functional groups react with the C—Mg bond and are not compatible with reagent formation; among these are groups with acidic hydrogens (unless the proton is first removed by metallation¹⁴¹); nitro-, carbonyl- and other unsaturated groups with polar character; and many carbon- and heteroatom-halogen compounds.

Nevertheless, if the reactions are conducted carefully, certain functional reagents can be prepared. 1,1-Di- or polyhalo compounds usually give no well-defined products with Mg metal; **they may even cause explosions** (see, however, the exception of the dihalomethanes, above).

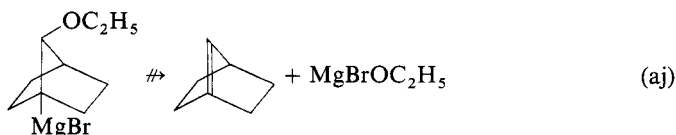
1-Alkoxymethylmagnesium halides can be obtained from the corresponding chloromethylalkyl ethers with special precautions; activation with HgCl_2 is recommended; DME¹⁴², Et_2O ¹⁴³ or THF¹⁴⁴ are used. The organomagnesium-halide reagents are usually formed and used at $<0^\circ\text{C}$ because they decompose at higher T:



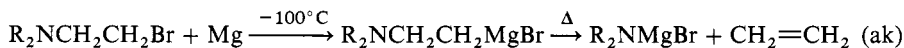
Analogous sulfur compounds are also prepared^{144,145}. 1,2-Dihalo compounds lead to the formation of alkenes (see above), as do 1-halo-2-X-substituted alkanes ($\text{X} = \text{NR}_2\text{OR}$, SR, etc.). In the aromatic series 2-heterosubstituted reagents can be stable¹⁴⁷, for elimination would lead to highly strained arynes. Similarly, the elimination reaction may be difficult when allenes¹⁴⁸:



or bridgehead double bonds¹⁴⁹ would be formed:



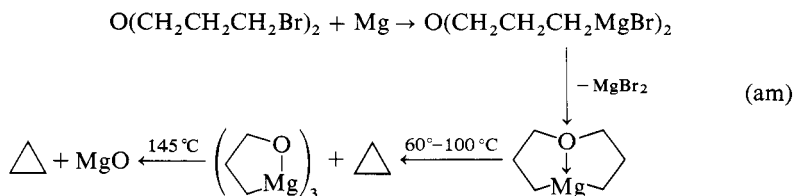
Simple β -aminoethylmagnesium bromides are prepared at -100°C with the aid of active Mg metal and are stable, depending on the substitution, from -90° to -20°C ¹⁵⁰:



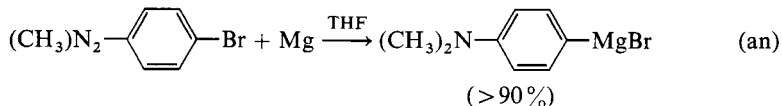
Except for the dihaloalkanes (see above), 3-heterosubstituted 1-haloalkanes yield the corresponding organomagnesium-halide reagents in a normal fashion^{44,151}:



However, 1,3 elimination can occur at elevated T, although the stability of the reagents is higher in solution than in the solid¹⁵²:



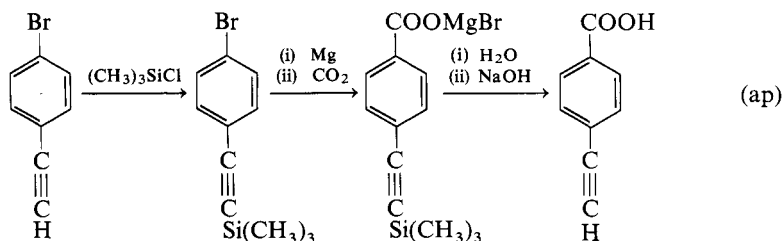
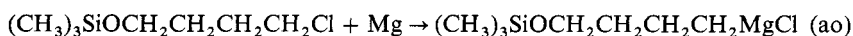
With \geq four carbon atoms between the halogen and the hetero function, the preparation of the organomagnesium-halide reagent is normal. If difficulties arise, they are often related to solubility problems, as illustrated by the reaction of 4-dimethylaminobromobenzene with Mg metal in Et_2O . It reacts with difficulty under entrainment with ethyl bromide¹⁵³, whereas in THF, the reaction proceeds smoothly¹⁵⁴:



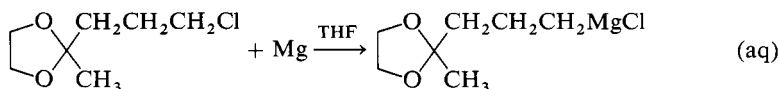
In the absence of other heteroatoms, organic halides containing Si¹⁵⁵, Ge¹⁵⁵, Sn¹⁵⁵ or As¹⁵⁶ react to form the organomagnesium-halide reagent like ordinary halides, even if only one carbon atom separates the halogen from the heteroatom. Methylsulfonyl¹⁵⁷ and carboranyl groups¹⁵⁸ are also compatible with an intramolecular magnesium-halide function.

Functional groups that react with C—Mg bonds can be protected to make them suitable for reaction. Again, heteroatoms should be at least three to four carbon atoms removed from the Mg.

Acidic hydrogens can be protected by alkylation, preferentially by an alkyl group that can be removed after the reaction. Benzyl, *t*-Bu and tetrahydropyranyl groups are most frequently used for OH and NH groups. The trimethylsilyl group is both stable and easily introduced and removed¹⁵⁹; it can even serve to protect C—H bonds, e.g.¹⁶⁰:

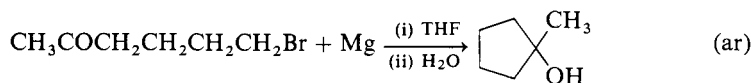


Aldehyde and keto functions may be protected in the usual way as 1,3-dioxolanes¹⁶¹:

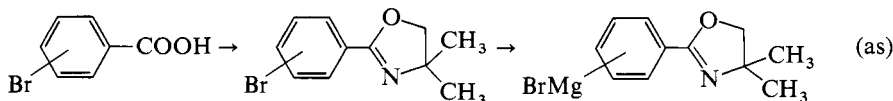


but in the absence of a strongly basic solvent, substituted 1,3-dioxolanes are attacked by organomagnesium-halide reagents¹⁶².

Without a protective group, the haloketones react with Mg intramolecularly by attack of the intermediate organomagnesium halide on the hetero function^{95,163}:

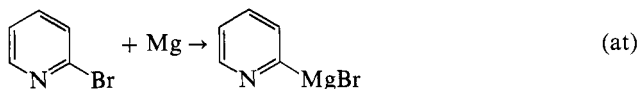


Carboxy groups may be protected by reaction with 2-amino-2-methylpropanol; the resulting 4,4-dimethyl-4,5-dihydro-1,3-oxazol is inert to organomagnesium halide reagents and can be removed by acid treatment¹⁶⁴:



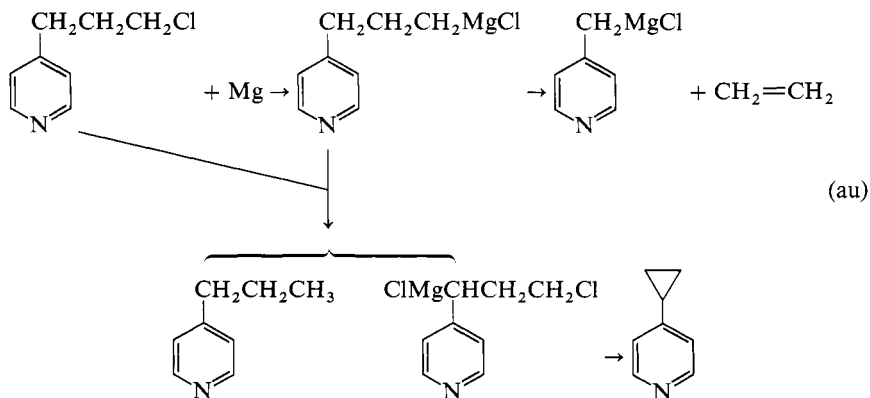
(vi) Heterocyclic Reagents. Heterocyclic compounds are in principle compatible with the organomagnesium-halide reaction. In particular, if the heterocycle is stabilized by aromaticity, it behaves as an aromatic rather than as a halogen derivative containing

nitrogen, oxygen or sulfur; e.g., 2- and 3-bromopyridine are transformed by entrainment (yield 78 %¹⁶⁵ and 79 %¹⁶⁶, respectively), even though they contain the nitrogen in α and β positions, respectively, to the metal:



Whereas halothiophenes react more readily than their benzene analogues, halofurans and halopyridines do so less easily. In Et_2O , entrainment is usually necessary, but in THF these difficulties often can be avoided. If more than one halogen atom is present, the reaction tends to be more sluggish; in Et_2O , entrainment is required and leads to mono reagents, whereas in THF occasionally bis-magnesium halide reagents are found. A compilation of heterocyclic organomagnesium-halide reagents is available¹⁶⁷.

Nitrogen-containing heterocycles can pose problems that are not encountered in their homocyclic analogues. Obviously, heterocycles involving NH groups, such as pyrrol and its annellated and aza derivatives, will destroy an organomagnesium-halide reagent formed from their halo derivatives. Another example is that of 4-(3-chloropropyl)pyridine¹⁶⁸ (and its homologues¹⁶⁸), which shows side reactions (Scheme 1) because of the stability of 4-pyridylmethyl anions.



Scheme 1

(F. BICKELHAUPT)

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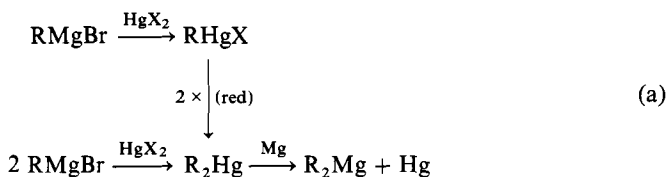
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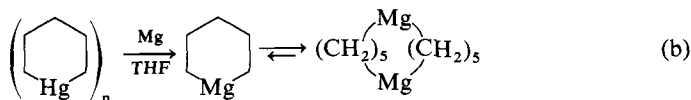
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167. Ref. 16, p. 127.
168. Ref. 16, p. 126, 132.

5.4.2.2.2. from Organomercury Compounds with the Metal.

This method is less useful preparatively because in most cases the required organomercurials are obtained by the reaction of organomagnesium-halide reagents with mercury(II) halides:



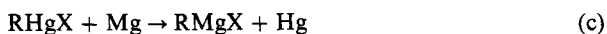
However, it can become the method of choice. First, it is superior for the preparation of diorganomagnesiums in a pure form. Usually, diorganomagnesiums are obtained from the corresponding organomagnesium-halide reagents by precipitation of MgBr_2 with dioxane (see §5.4.2.3.2.). In this approach, impurities in the organomagnesium halide reagents are normally retained, and traces of MgBr_2 or of dioxane are difficult to remove, e.g., in the preparation of pure magnesacyclohexane (which tends to form the 12-membered ring dimer)^{1,2}:



Second, this approach may be necessary when the corresponding organomagnesium-halide reagents are not available via the direct method.

Organomercury derivatives can be extremely toxic, and appropriate precautions should be taken in handling them. The metal-exchange reaction usually proceeds smoothly and in nearly quantitative yield. In coordinating solvents, such as Et_2O or tetrahydrofuran (THF), it can be performed by stirring or shaking Mg turnings with the diorganomercurial, which does not need to be completely dissolved. At RT, a few hours or days are required for the reaction to go to completion. In the absence of such solvents³, higher T are needed (60–90°C), in particular for diarylmercurials (150°C).

Metal exchange is not limited to diorganomercurials but can also be performed with organomercury halides:



5.4. Formation of Bonds between Elements

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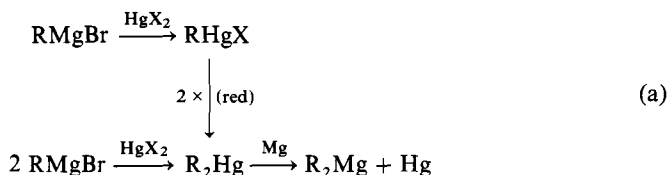
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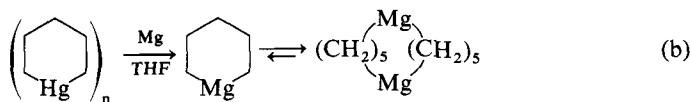
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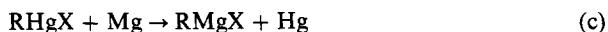
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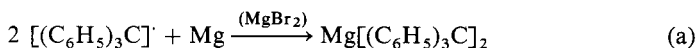
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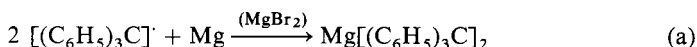
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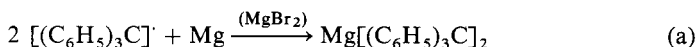
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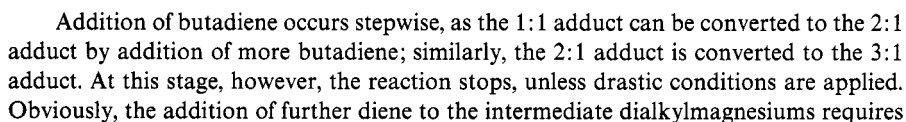
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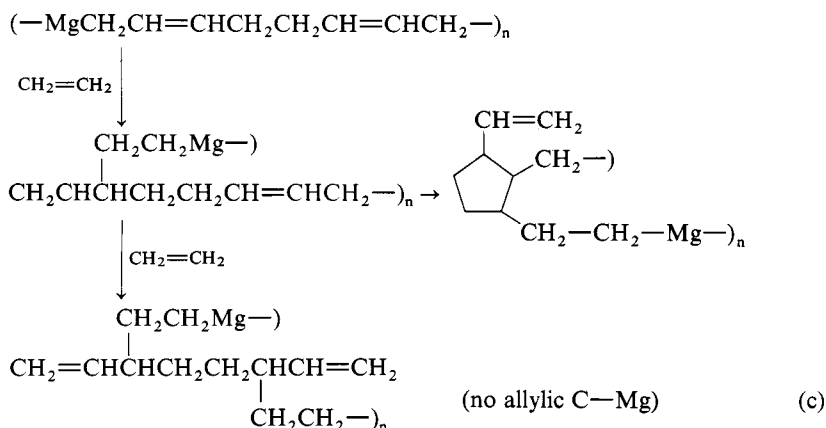
Usually, a strongly electron-donating solvent such as tetrahydrofuran (THF) or hexamethylphosphoramide (HMPA) and (slightly) elevated T are required; alkyl halides and alkylmagnesium halides, often in combination with transition-metal salts, are catalysts. In most cases, the addition of Mg occurs with formation of dimeric or oligomeric adducts.

$$\begin{array}{c}
 2 \text{ C}_6\text{H}_5\text{CH}=\text{CH}_2 + \text{Mg} \rightarrow \left[\text{C}_6\text{H}_5 - \text{C}(\text{Mg}) - \text{CH}_2 - \text{C}_6\text{H}_5 \right]_n \\
 \downarrow \begin{array}{c} \text{(i) } 2 \text{ CO}_2 \quad \text{(ii) } \text{H}_2\text{O} \end{array} \\
 \begin{array}{c} \text{COOH} \quad \quad \text{COOH} \\ | \quad \quad | \\ \text{C}_6\text{H}_5\text{CHCH}_2\text{CH}_2\text{CHC}_6\text{H}_5 \end{array}
 \end{array} \quad \text{(a)}$$

Conjugated 1,3-dienes, such as butadiene, isoprene, dimethylbutadienes and certain monoterpenes, undergo this addition-dimerization reaction even more readily^{3,4}. The ratio of products depends⁵ on the ratio of diene to Mg. With a diene:Mg $\leq 1:1$, a 1:1 adduct is the main product; with ratios of 2:1 and 3:1, 2:1 adducts and 3:1 adducts are the main products:

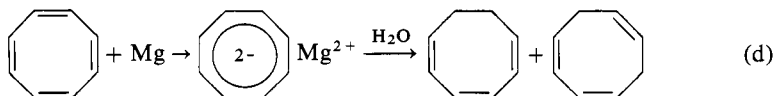


the presence of allylic C—Mg units, which insert into C—C bonds⁶; even ethylene is added^{7,8} to the products of butadiene and Mg:

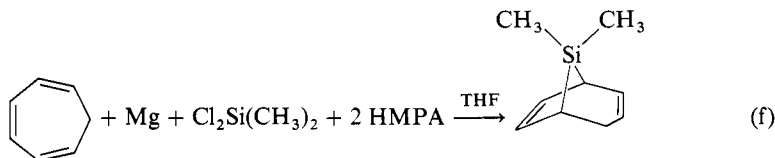
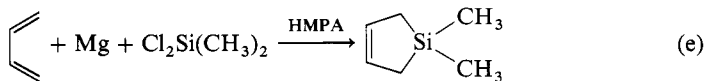


The higher adducts in these reactions form cyclization products. These no longer contain the allylic C—Mg unit, which explains why the reaction stops at the 3:1 adduct stage.

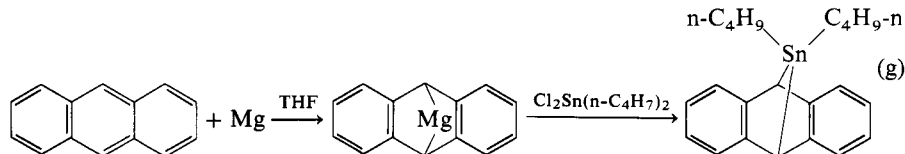
Magnesium adds to cyclooctatetraene in THF; MgBr_2 catalyzes the reaction⁹. The adduct yields other organometallic derivatives of cyclooctatetraene; on hydrolysis, 1,3,5- and 1,3,6-cyclooctatriene are formed:



The addition may also be performed in the presence of a third reaction partner¹⁰, which converts the adduct directly to the desired end product; e.g., butadiene reacts with Mg metal and dimethyldichlorosilane in HMPA to give 1,1-dimethylsilacyclopent-3-ene¹¹, and with cycloheptatriene a bicyclic Si compound is obtained¹²:



A second class of conjugated hydrocarbons that react with Mg metal is bi- and polynuclear aromatics. Anthracene, chrysene and pyrene react in THF (catalyzed by $n\text{-C}_4\text{H}_9\text{Cl}$ and CH_3I ¹³); the Mg-anthracene adduct can be isolated^{14,15}:



Dinuclear aromatics, such as naphthalene, biphenyl and fluorene (and likewise phenanthrene and anthracene), add Mg only in more basic solvents, such as HMPA or NH_3 . Magnesium dissolves in HMPA to give a blue solution that converts the aromatics to the adducts¹⁶. It may be advantageous to prepare the adducts in NH_3 first and then replace this solvent by HMPA¹⁷. The green adducts obtained in NH_3 are resistant to ammonolysis. On hydrolysis, the naphthalene adduct forms 1,4-dihydronaphthalene (besides naphthalene, tetralin and bis-2-tetralyl); with 2:1 xs Mg, only tetralin and bis-2-tetralyl are formed¹⁸. Similarly, the biphenyl-Mg adduct yields 1-, 3- and 4-phenylcyclohexene on hydrolysis¹⁹.

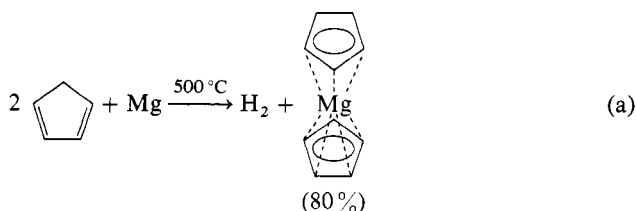
(F. BICKELHAUPT)

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17. J. P. Pascault, J. Golé, *C. R. Hebd. Seances Acad. Sci.*, **C264**, 115 (1967).
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19. P. Markov, L. Dimitrova, C. Ivanov, *Monatsh. Chem.*, **107**, 619 (1976).

5.4.2.2.5. from Acidic Hydrocarbons to Evolve H_2 .

Acidic hydrocarbons can be converted to the corresponding diorganomagnesiums by the action of Mg metal. Although in principle this reaction should be applicable to hydrocarbons with a $\text{pK}_\text{A} \approx 20$, the only example is that of cyclopentadiene and its methyl derivative.

The preparation of dicyclopentadienylmagnesium¹ uses a specially designed apparatus in which dicyclopentadiene is depolymerized by heating to 160°C. Cyclopentadiene is carried by a stream of N_2 to the top of a vertical borosilicate glass reactor that is filled with Mg turnings and heated to 500°C. Dicyclopentadienylmagnesium (mp 177°C) sublimes to the bottom, where it is collected (yield 80% of reacted cyclopentadiene):



5.4. Formation of Bonds between Elements

257

5.4.2. Formation of the Carbon—Mg Bond

5.4.2.2. from Mg Metal and its Alloys

Dinuclear aromatics, such as naphthalene, biphenyl and fluorene (and likewise phenanthrene and anthracene), add Mg only in more basic solvents, such as HMPA or NH_3 . Magnesium dissolves in HMPA to give a blue solution that converts the aromatics to the adducts¹⁶. It may be advantageous to prepare the adducts in NH_3 first and then replace this solvent by HMPA¹⁷. The green adducts obtained in NH_3 are resistant to ammonolysis. On hydrolysis, the naphthalene adduct forms 1,4-dihydronaphthalene (besides naphthalene, tetralin and bis-2-tetralyl); with 2:1 xs Mg, only tetralin and bis-2-tetralyl are formed¹⁸. Similarly, the biphenyl-Mg adduct yields 1-, 3- and 4-phenylcyclohexene on hydrolysis¹⁹.

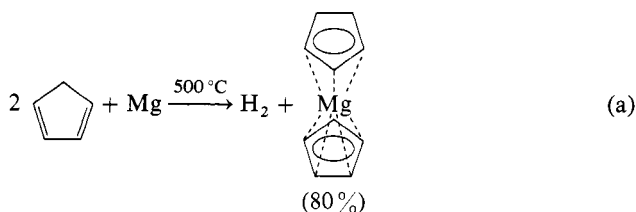
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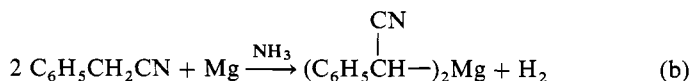
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Purification can be achieved by resublimation (subl. 100°C, 1 bar)². Under similar conditions, methylcyclopentadiene yields a mixture of dicyclopentadienylmagnesium and bis(methylcyclopentadienyl)magnesium³. With catalytic amounts of cyclopentadienyltitanium trichloride this reaction can be performed at 0°C within 48 h⁴. Dicyclopentadienylmagnesium can also be prepared by sublimation [250°C, 10⁻⁴ torr (10⁻⁷ bar)] of cyclopentadienylmagnesium bromide⁵.

Triphenylmethane (pK_a = 31) is not sufficiently acidic; it is not metallated by Mg metal in Et₂O⁶. On the other hand, C—H bonds that are strongly activated by carbanion-stabilizing groups can be metallated directly, as illustrated by the reaction of phenylacetonitrile with Mg metal in liquid NH₃⁷:



Toluene is a side product (40%).

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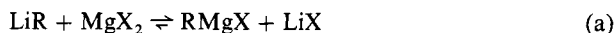
1. W. A. Barber, *Inorg. Synth.*, **6**, 11 (1960).
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5.4.2.3. from Magnesium Halides

5.4.2.3.1. by Reaction with Group-IA Organometallics.

Organometallics MR (M = Li, Na, K)¹ are transformed into organomagnesiums by reactions with anhydr MgX₂ (X = Cl, Br, I). Anhydrous MgX₂ may be obtained (see §2.7) by dehydration² of hydrated double salts of MgX₂ with NH₄X (X = Cl, Br) or MgI₂·8H₂O in an atmosphere of HX, or from³ Mg metal with HgX₂ (X = Cl, Br, I) in refluxing tetrahydrofuran (THF) or Et₂O. Activated MgCl₂, necessary for some preparations, precipitates when s-BuMgCl reacts with BzCl or Cl₂ or when Mg metal reacts with n-C₅H₁₁Cl^{4,5} or ClCH₂CH₂Cl⁶, and may also be obtained⁴ by treatment of commercial MgCl₂ with i-PrOH. Anhydrous MgBr₂ is prepared from Mg and 1,2-dibromoethane in Et₂O or THF and may be used in situ^{2,3,6}. Anhydrous MgI₂ may be formed from Mg and I₂ in ethers².

(i) Reactions with Organolithiums. The interconversion¹ of LiR into corresponding organomagnesium halide reagents:



proceeds to completion in ethers as established by reactivity tests⁷ on the product when R = p-Me₂NC₆H₄, n-Bu, X = I and by ¹H NMR when⁸ R = Me, X = Br. Nevertheless, the presence of LiX may influence subsequent reactions of the organomagnesium-halide reagent, and addition of xs LiX may displace the equilibrium partially to form^{7,8} some LiR.

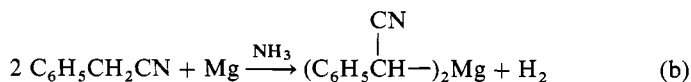
5.4. Formation of Bonds between Elements

5.4.2. Formation of the Carbon—Mg Bond

5.4.2.3. from Magnesium Halides

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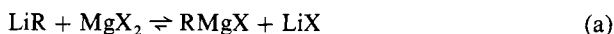
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(i) Reactions with Organolithiums. The interconversion¹ of LiR into corresponding organomagnesium halide reagents:



proceeds to completion in ethers as established by reactivity tests⁷ on the product when R = p-Me₂NC₆H₄, n-Bu, X = I and by ¹H NMR when⁸ R = Me, X = Br. Nevertheless, the presence of LiX may influence subsequent reactions of the organomagnesium-halide reagent, and addition of xs LiX may displace the equilibrium partially to form^{7,8} some LiR.

In general, RMgX is prepared¹ by stirring LiR with 1 equiv (or a slight xs) of MgX_2 ($\text{X} = \text{Br}, \text{I}$) in Et_2O or THF at or below RT for up to 1 h; heat evolved in reaction (a) may cause Et_2O to reflux. Examples of organomagnesium-halide reagents formed by this method are listed in Table 1.

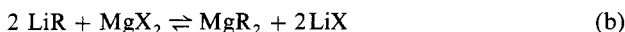
The LiR derivatives may be prepared by exchange between an organic precursor and an available alkyl lithium compound, whereas such an organic group exchange is less facile for organomagnesium-halide reagents. Reaction (a) is useful when direct interaction of RX with Mg metal is sluggish, especially in Et_2O ⁹; e.g., for $\text{R} = \text{p-Me}_2\text{NC}_6\text{H}_4$ ⁷, 9-triptycyl¹⁰, 3-thienyl¹¹ and substituted vinyl¹². The synthesis of *o*-di(bromo-magnesium)benzene (88%) from *o*- $\text{Li}_2\text{C}_6\text{H}_4$ is possible¹³, and perfluoroorgano-magnesium-halide reagents are also formed² from LiR_f ($\text{R}_f = \text{perfluoroalkyl}$) and MgI_2 .

Exchange of (R)-1-methyl-2,2-diphenylcyclopropyllithium with MgBr_2 affords (S)- $\text{Ph}_2\text{CCH}_2\text{CMe}(\text{MgBr})$ with retention of configuration¹⁴. This product is a rare example of an optically active organomagnesium-halide reagent with chirality at the α -C atom (acyclic reagents undergo inversion of the $\text{Mg}-\text{C}$ bond).

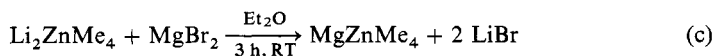
A cyclic reagent which undergoes diastereoselective reactions, 1-bromomagnesium-N-pivaloyltetrahydroisoquinoline, is also obtained¹⁵ by exchange from the corresponding Li reagent and forms a structurally characterized tris-THF adduct.

Formation of polymeric organomagnesium-halide reagents by reaction (a) is possible. The propagation of styrene to the so-called living polymer is conveniently carried out using LiR . The resultant polystyryllithium, $\text{R}-(\text{PhCHCH}_2)_n\text{Li}$, may be converted into less reactive $\text{R}-(\text{PhCHCH}_2)_n\text{MgBr}$ by reaction with MgBr_2 in THF¹⁷.

The equilibrium involving 2:1 LiR and MgX_2 :



also lies, from the $^1\text{H-NMR}$ studies, to the right when $\text{R} = \text{Me}$, $\text{X} = \text{Br}$ in Et_2O , although the presence of LiX and traces of LiMe may explain some abnormal reactivity of the product⁸, MgR_2 . Diarylmagnesiums are prepared by reaction (b) in ether or THF⁶. The 2:1 ate complex of LiMe and ZnMe_2 with MgBr_2 forms the Mg-Zn derivative¹⁵:



but the product is in dynamic equilibrium with the binary constituents, MgMe_2 and ZnMe_2 .

Reaction of activated MgCl_2 with alkylolithiums in hydrocarbons occurs according to Eq. (b) when MgR_2 is a hydrocarbon-soluble product. In benzene-cyclohexane, xs MgCl_2 reacts exothermically with LiBu-s to yield an $\text{Mg}(\text{Bu-s})_2$ solution (0.25 h, $\leq 95\%$)⁴ after removal of LiCl and MgCl_2 by centrifugation. Activated MgCl_2 also reacts with 5,5-dimethylhex-2-enyllithium (prepared by addition of LiBu-t to 1,3-butadiene) in *n*-pentane at RT to form soluble $\text{Mg}(\text{CH}_2\text{CH}=\text{CHCH}_2\text{CMe}_3)_2$ (overall yield 70%, 1 h)⁵. Similarly, preparations of MgR_2 ($\text{R} = \text{n-Bu}, \text{i-Bu}, \text{t-Bu}, \text{n-C}_5\text{H}_{11}$) according to Eq. (b) ($\text{X} = \text{Cl}$) are possible by stirring the reagents in benzene containing Et_2O ($< 2 \text{ mol } \%$)¹⁹. A useful cyclic process for manufacture of MgR_2 ($\text{R} = \text{Bu}, \text{n-C}_5\text{H}_{11}$) is initial reaction between RCl and Mg metal in hydrocarbon solvent:



TABLE 1. PREPARATION OF ORGANOMAGNESIUMS FROM ORGANOLITHIUM DERIVATIVES AND ANHYDROUS MAGNESIUM HALIDES

LiR	MgX ₂	Solvent ^a	Product	Refs.
LiBu-n	MgI ₂	Et ₂ O	n-BuMgI	7
LiCMe=CHR ^b	MgBr ₂	THF (−50°C)	RCH=CMg(MgBr)	12
Ph ₂ CCH ₂ CMgLi	MgBr ₂	Et ₂ O	Ph ₂ CCH ₂ CMg(MgBr)	14
HC(o-C ₆ H ₄) ₃ Cl ^c	MgI ₂	THF (reflux)	HC(o-C ₆ H ₄) ₃ CMgI	10
p-Me ₂ NC ₆ H ₄ Li	MgI ₂	Et ₂ O	p-Me ₂ NC ₆ H ₄ MgI	7
3-LiC ₆ H ₃ S ^d	MgBr ₂	Et ₂ O	3-C ₆ H ₃ S(MgBr)	11
o-Li ₂ C ₆ H ₄	MgBr ₂	Et ₂ O	o-C ₆ H ₄ (MgBr) ₂	13
LiCH ₂ (CH=CH) ₂ SiMe ₃	MgBr ₂	THF (0°–25°C)	Me ₃ Si(CH=CH) ₂ CH ₂ MgBr	16
R(−PhCHCH ₂) _n Li ^e	MgBr ₂	THF	R(−PhCHCH ₂) _n MgBr	17
LiBu-s	MgCl ₂	Benzene-cyclohexane	s-Bu ₂ Mg	4
LiBu-n	MgCl ₂	Benzene (+2% Et ₂ O)	n-Bu ₂ Mg	19
LiCH ₂ CH=CHCH ₂ CMe ₃	MgCl ₂	n-pentane	Mg(CH ₂ CH=CHCH ₂ CMe ₃) ₂	5
LiC ₈ H ₄ Me-o	MgCl ₂ ·n THF	Et ₂ O	Mg(C ₈ H ₄ Me-o) ₂	6
Li ₂ ZnMe ₄	MgBr ₂	Et ₂ O	MgZnMe ₄	18
Li ₂ (CH ₂ CHCHS) ^f	MgBr ₂ ·Et ₂ O	THF (0°C)	Mg(CH ₂ CHCHS)	24
RCO(Me)N(CHCHCH ₂)Li ^g	MgBr ₂ ·Et ₂ O	THF (> −85°C)	RCO(Me)N(CHCHCH ₂)MgBr	25
PhCH=CLi(SO ₂ Ph)	MgBr ₂ ·Et ₂ O	Benzene-THF-Et ₂ O (< −45°C)	PhCH=C(MgBr)(SO ₂ Ph)	26
1-LiC ₈ H ₅ NCOBu-t ^h	MgBr ₂ ·Et ₂ O	THF (−78°–0°C)	1-BrMgC ₈ H ₅ N(COBu-t)	15

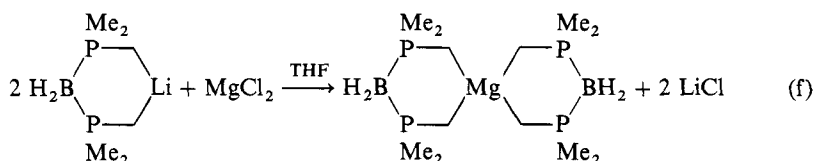
^a At RT unless otherwise stated.^b R = t-BuSiMe₂OCHEtCHMe.^c 9-Triptycylithium.^d 3-Thienyllithium.^e Polystyryllithium.^f Dilithium-*thioacrolein* dianion with 2 equiv tetramethylethylenediamine (TMED).^g R = CMe₂CH₂(OCCH₂CH₂O)CCH₂CMe₂N.^h 1-Lithio-N-pivaloyltetrahydroisoquinoline.

followed by alkylation of MgCl_2 with LiR (Eq. b) and the reformation of LiR from LiCl using RCl and Na metal²⁰. The solubility of $\text{Mg}(\text{Bu-n})_2$ in hydrocarbons is increased ($>0.7\text{N}$ in *n*-alkanes) by the presence of equimol $\text{Mg}(\text{Bu-s})_2$ and also 10% $\text{Mg}(\text{n-octyl})_2$ ²¹; *n*-BuCl and $\text{C}_8\text{H}_{17}\text{Cl}$ (9:1) are introduced initially [Eq. (d)] and then $\text{Mg}(\text{Bu-s})_2$ is formed by alkylation of the resulting MgCl_2 with LiBu-s . Related reactions involve the alkylation of organomagnesium-halide reagents by LiR in Et_2O or $\text{Et}_2\text{O-cyclohexane}$:

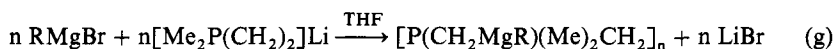


e.g., $\text{R} = \text{R}' = \text{Bu}$, *i*-Bu, *s*-Bu, *t*-Bu, $\text{n-C}_5\text{H}_{11}$; $\text{R} = \text{Me}$, $\text{R}' = \text{i-Bu}$; $\text{R} = \text{s-Bu}$, $\text{R}' = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$ ¹⁹.

A spirocyclic compound is synthesized (43%)²²:

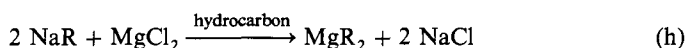


and a related phosphorus ylide organometallic is obtained ($\text{R} = \text{Me}$, Et)²³:

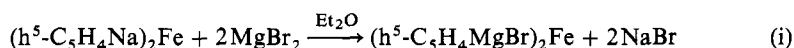


Dilithium derivatives of delocalized dianions of thioacrolein and $\text{Li}_2(\text{CH}_2\text{CRCHS})$ homologues, formed by metallation of the corresponding allylmercaptans in the presence of 2 equiv tetramethylethylenediamine (TMED) react with $\text{Br}_2\text{Mg}\cdot\text{OEt}_2$ in THF (0°C , 10–15 min) to give synthetically useful species, $\text{Mg}(\text{CH}_2\text{CRCHS})$ ($\text{R} = \text{H}$, Me), in high yield²⁴. A related allylic magnesium-halide reagent, $\text{RCO}(\text{Me})\text{N}(\text{CHCHCH}_2)\text{MgBr}$ ($\text{R} = \text{CMe}_2\text{CH}_2(\text{OCH}_2\text{CH}_2\text{O})\text{CCH}_2\text{CMe}_2\text{N}$), is formed by exchange, [see Eq. (a)], between the corresponding lithiated allylurea and $\text{Br}_2\text{Mg}\cdot\text{OEt}_2$ in THF ($> -80^\circ\text{C}$)²⁰. α -Lithiovinylsulfones, $\text{RCH}=\text{CLi}(\text{SO}_2\text{Ph})$, react with $\text{Br}_2\text{Mg}\cdot\text{OEt}_2$ in mixed benzene-ether at -80° to -45°C to form $\text{RCH}=\text{C}(\text{MgBr})(\text{SO}_2\text{Ph})$ ($\text{R} = \text{Me}$, Ph)²¹.

(ii) Reactions with Organosodiums. Exchange between NaR and MgX_2 ($\text{X} = \text{Cl}$, Br , I) form organomagnesiums, but simple organosodiums, being less readily prepared than LiR , are little used for synthetic purposes; NaR compounds with unsaturated R groups are more useful. However, NaR ($\text{R} = \text{Bu}$, Ph , formed from Na dispersion in isooctane and RCl ; $\text{R} = \text{Ph}_3\text{C}$, from NaBu and Ph_3CH) reacts with MgCl_2 in hydrocarbons in a ball mill to give MgR_2 in yields of 60–90% as determined by carbonation²²:



Although 1,1'-dibromoferrocene, $(\text{h}^5\text{-C}_5\text{H}_4\text{Br})_2\text{Fe}$, reacts directly with Mg metal in THF, the bis-organomagnesium-bromide reagent is not easily synthesized. An alternative route to $(\text{h}^5\text{-C}_5\text{H}_4\text{MgBr})_2\text{Fe}$ involves metallation of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Fe}$ with NaR ($\text{R} = \text{C}_5\text{H}_{11}$ or Ph) to give red $(\text{h}^5\text{-C}_5\text{H}_4\text{Na})_2\text{Fe}$. The exchange:

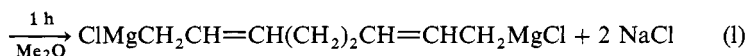
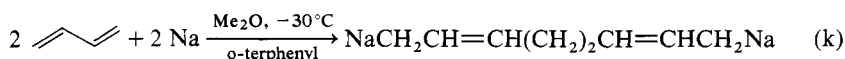


occurs²⁸ on stirring 1 h at RT. The yellow product may be converted²⁸ to dicarboxylic acid (30%) by carbonation with CO₂.

Styrene in Me₂O-i-C₈H₁₈ at -40° to +40°C dimerizes in the presence of Na metal and o-terphenyl to form the dianion (4 h), and this reacts subsequently on addition²⁹ of MgCl₂:

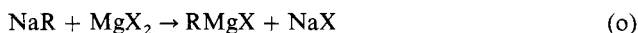
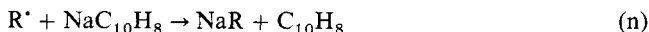
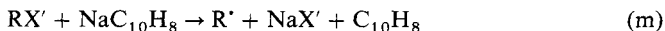


This process may also be carried out in one step by adding MgCl₂ during the first stage²⁹. A related preparation is the conversion of butadiene to 1,8-bis(chloromagnesio)-octa-2,6-diene³⁰:



A similar exchange may be used to make bis-organomagnesium-halide reagents from dianionic living polymers of butadiene initiated by electron transfer from Na naphthalene¹⁷.

Sodium naphthalene, NaC₁₀H₈, reduces MgCl₂ in THF to produce an activated form of Mg metal that may be employed in direct preparation of organomagnesium-halide reagents³¹. However, NaC₁₀H₈ is also useful for preparing reagents from RX' in the presence of MgX₂ in THF; the yields of such reactions are sometimes better than from the direct method using activated Mg and the stereochemistry of the two processes may differ. The reactions proceed via an organosodium intermediate by a radical mechanism:



The formation of radical R' explains the lack of stereoselectivity in formation of RMgX (X = Cl, Br) from anti- and syn-7-halogenobenzonorbornadiene, but yields vary (<95% from anti-RX; 32–36% from syn)³². This method also may be applied when R = n-hexyl (85%)³³ and R = norborn-2-en-7-yl (yield of syn + anti RMgX is >19%)³⁴. A solution of NaC₁₀H₈ in THF is added dropwise to RX and MgX₂ (X = Cl, Br) in THF, and at the end point of the reaction the deep-green color of NaC₁₀H₈ persists^{32–34}.

Sodium anthracene reacts with MgBr₂ in THF to produce green-yellow solutions from which MgC₁₄H₁₀·3 THF may be crystallized³⁵.

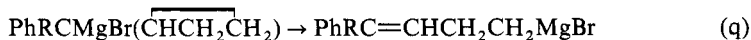
(iii) Reactions with Organopotassiums. In preparing Ph₂CHMgBr from Mg metal with Ph₂CHX (X = Cl, Br), a major product is Ph₂CHCHPh₂, resulting from coupling. Alternatively, the organomagnesium-halide reagent can be prepared in solution from

readily obtained Ph_2CHK by stirring with MgBr_2 in Et_2O until the red color is dispelled ($\text{R} = \text{H}$, $\leq 90\%$)^{36,37}; no coupled product is formed:



The Ph_2CHK can be obtained³⁶ by metallation of Ph_2CH_2 with KNH_2 in liq NH_3 or, more conveniently³⁷, by metallation of the hydrogen in benzene using KOBu-t-LiBu-n . A related synthesis may be employed for Ph_3CMgBr (Eq. p), $\text{R} = \text{Ph}$; the low yield of Ph_3CMgBr in solution (ca. 20%) is attributable to its poor solubility³⁷ in Et_2O . Similarly, phenylallylpotassium, $\text{K}[\text{CH}_2\text{CH}=\text{CHPh}]$, obtained by metallation of allylbenzene with KOBu-t-LiBu-n , reacts with MgBr_2 in Et_2O ; giving³⁷ soluble $\text{PhCH}=\text{CHCH}_2\text{MgBr}$.

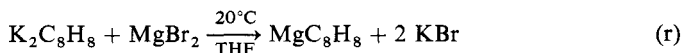
Cleavage of the C—O bond in aralkylmethylethers, PhRR'COME , by Na—K alloy in Et_2O or THF also yields benzylic organopotassium precursors, PhRR'CK . When $\text{R} = \text{R}' = \text{Me}$, $\text{PhMe}_2\text{CMgBr}$ may be obtained in Et_2O by subsequent exchange³⁷ with MgBr_2 . When $\text{R} = \text{Ph}$, $\text{R}' = \text{cyclopropyl}$ or $\text{R} = \text{R}' = \text{cyclopropyl}$ in Et_2O (or THF), the organomagnesium-halide reagent first formed on addition of MgBr_2 undergoes an immediate ring-opening rearrangement³²:



Carbocation with solid CO_2 gives the acid $\text{PhRC}=\text{CHCH}_2\text{CH}_2\text{COOH}$ ($\text{R} = \text{Ph}$, 63%; $\text{R} = \text{C}_3\text{H}_5$, 70%)³⁸.

Methylcyclopentadienylpotassium or -sodium does not form $\text{Mg}(\text{C}_5\text{H}_4\text{Me})_2$ by reaction with anhydr Mg salts in Et_2O or THF². Nevertheless, a range of bis(dienyl)-magnesium compounds MgR_2 is formed by reaction of 2:1 KR with MgBr_2 in THF³⁹. When $\text{R} = \text{RCH}=\text{CR'CR''}=\text{CR'''CH}_2$ (R , R' , R'' , R''' being various combinations of H and Me) or $\text{R} = \overline{\text{CH}=\text{CH}(\text{CH}_2)_n\text{CH}=\text{CH}-\text{CH}}$ ($n = 2, 3$) the products are obtained by stirring KR with MgBr_2 at 10°C (3 h). Products may be obtained as solvates $\text{MgR}_2(\text{THF})_2$ ($\leq 95\%$) and complexes $\text{MgR}_2(\text{TMED})$ are formed by addition of TMED in pentane to the product in THF³⁹. By reacting 1:1 potassium dienide and MgBr_2 the reagents RMgBr are formed³⁹.

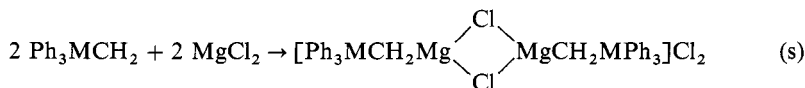
Cyclooctatetraenemagnesium is synthesized by reaction:



The product forms a solvate $\text{Mg}(\text{C}_8\text{H}_8) \cdot 2.5 \text{ THF}$, which is insoluble in THF⁴⁰.

Potassium metal with MgX_2 , especially MgCl_2 in the presence of KI, is used to produce a highly reactive form of Mg metal that is effective in reacting with less active organic halides, including RF ⁴¹ (see §5.4.2.2.1), but organopotassiums are not involved. Reduction of MgI_2 with potassium graphite, C_8K , in refluxing Et_2O or benzene forms a lamellar intercalation compound of Mg with graphite, $\text{C}_{16}\text{Mg}(\text{KI})_2$, which is active for preparations of organomagnesium-halide reagents from organic halides⁴².

(iv) Reactions with Alkylidenetriphenylphosphoranes or -arsoranes. Reactions of 4:1 $\text{Ph}_3\text{P}=\text{CH}_2:\text{MgCl}_2$ in THF yields the dimeric salt $[\text{Mg}_2\text{Cl}_2(\text{CH}_2\text{PPh}_3)_2]\text{Cl}_2$ in 73.2% yield which is soluble in polar solvents⁴³:



where M = P, As. A related arsenic derivative (M = As; 88.3% yield) is obtained from 1:1 $\text{Ph}_3\text{As}=\text{CH}_2$: MgCl_2 .

(W. E. LINDSELL)

1. Group-IA organometallics are denoted by the formula MR, although associated forms may predominate, and organomagnesium-halide reagents by RMgX , although species in equilibria are present in solution (see also §5.4.2.3.2.) and W. E. Lindsell, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, Vol. 1, 1984, Ch. 4.
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9. By using appropriate activation and/or solvent most organic halides will react with Mg metal (see §5.4.2.2.1).
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43. Y. Yamamoko, *Bull. Chem. Soc. Jpn.*, 56, 1772 (1983); 57, 2835 (1984).

5.4.2.3.2. by Redistribution with Diorganomagnesium.

In solution, organomagnesium-halide reagents comprise several molecular species in dynamic equilibrium¹. Over a wide concentration range in tetrahydrofuran (THF)¹, and also in Et₃N², hexamethylphosphoramide (HMPA)³ and related polar solvents, monomeric solvated species are involved in the equilibrium (X = Cl, Br, I):



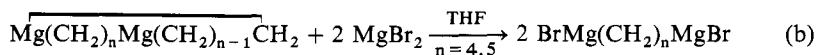
Equilibrium constants in THF are 1–10, so that all entities of Eq. (a) are present in significant concentrations. At low concentrations in Et₂O (<0.1 mol dm⁻³) similar monomeric solvated derivatives are present when X = Br, I, but when X = Cl dimeric forms prevail; at higher concentrations in Et₂O and related less polar solvents, associated forms (dimers, trimers, etc.) are in equilibrium with the monomeric species of Eq. (a). In Et₂O¹, as in Et₃N (X = Cl, Br)² and HMPA³, equilibria favor the mixed form RMgX (or associated analogue). Additionally, there is some ionization¹, especially in polar solvents, such as HMPA⁴.

Ready interchange of alkyl (R) and halogeno (X = Cl, Br, I) groups in Eq. (a) is established by ¹H NMR^{1,3,5} and by isotopic exchange¹; the rate of exchange is slower in more coordinating solvents. Thus, equimolar MgR₂ and MgX₂ (X = Cl, Br, I), both of which are actual components of organomagnesium halide reagents, redistribute to form an equilibrium mixture equivalent to a stoichiometric RMgX reagent; however, some organomagnesium-halide solutions prepared by direct reaction do not have stoichiometries corresponding to RMgX and may be either alkyl or halide rich.

Organomagnesium-fluoride reagents, (RMgF)₂, are dimeric in THF and Et₂O and the mobile equilibrium (Eq. a) does not exist there⁶. Redistribution between anhyd MgF₂ and MgR₂ (R = Me, Et) in Et₂O or THF does not occur even after refluxing 3 days⁶.

Equimolar MgEt₂ and anhyd MgBr₂ interact in Et₂O at RT to give solutions corresponding to those obtained from EtBr and Mg in the same medium; both solutions react identically with ketones and 1-hexyne and have identical physical properties, including degree of association, conductivity, dielectric constant and various spectra¹. Distinct breaks in thermometric titration curves⁷ and in variation of dielectric constants¹ as a function of MgEt₂ or MgBr₂ occur at 1:1 mixture and support formation of species of composition RMgX, and physical data of MgR₂ and MgX₂ systems in Et₂O (R = Me, Et, n-Bu, Ph, X = Br; R = Et, Ph, X = I)^{7,8} agree, with ΔH for redistribution = -8.4 to -20.6 kJ mol⁻¹. Hence, mixing MgR₂ in Et₂O with MgX₂ (X = Br, I and, probably Cl) affords the RMgX reagent.

Equimolar MgR₂ and MgX₂ (R = Et, n-Bu, Ph, X = Br; R = Et, Ph, X = Cl) in THF at RT are indistinguishable from the corresponding RMgX reagents^{8,9}. Enthalpy changes for redistribution are positive, (ΔH ≈ 11–25 kJ mol⁻¹) but entropy changes are larger than in Et₂O⁹. Thus, RMgX reagents are formed on mixing 1:1 MgR₂ and MgX₂ (X = Cl, Br, I) in THF. A secondary reaction between MgEt₂ and MgCl₂ in THF forms an organomagnesium of composition⁹ EtMg₂Cl₃ related to solid (EtClMg₂·3 THF)₂ obtainable by selective crystallization of the product from reaction of EtCl and Mg metal.^{1,10} Preparative applications in THF include¹¹:



5.4. Formation of Bonds between Elements

265

5.4.2. Formation of the Carbon—Mg Bond

5.4.2.3. from Magnesium Halides

42. C. Ungureanu, M. Palie, *Synth. React. Inorg. Metal-Org. Chem.*, 7, 581 (1977).43. Y. Yamamoko, *Bull. Chem. Soc. Jpn.*, 56, 1772 (1983); 57, 2835 (1984).**5.4.2.3.2. by Redistribution with Diorganomagnesium.**

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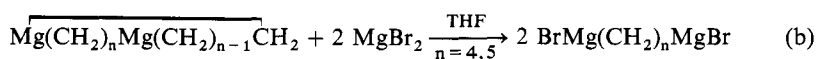
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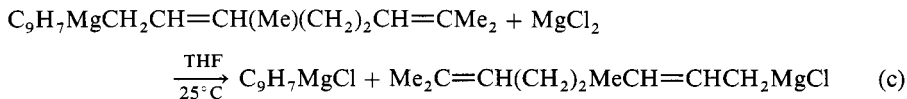
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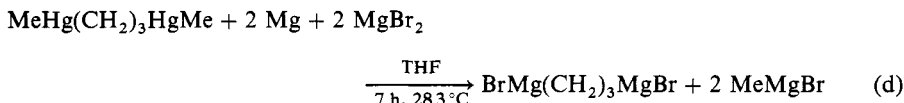
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and (C_9H_7 = indenyl)¹²:



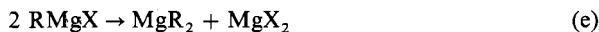
A useful route to 1,3-di(bromomagnesio)propane (98 %) involves reaction of $MgBr_2$ with the dialkylmagnesium formed from an organomercurial¹³:



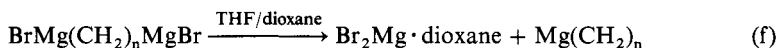
Redistribution of groups in MgR_2 ($R = Me, Et$) and MgX_2 ($X = Br, I$) occurs at RT in Et_3N , forming solvated² $RMgX$. Also, $Br_2Mg \cdot TMED$ and $Me_2Mg \cdot TMED$ complexes equilibrate in either Et_2O or benzene solution at RT, forming $MeBrMg \cdot TMED$. In hydrocarbons, $RMgX$ reagents obtained from RX and Mg are alkyl rich; the $R:X$ ratio in soluble organometallic products varies from $\approx 3-5$ ($X = I$) to ≈ 30 ($X = Cl$) so that MgR_2 species predominate^{1,14}. Addition of xs anhydr $MgBr_2$ to $(n-C_5H_{11})_2Mg$ in *n*-pentane (prepared from $n-C_5H_{11}Br$ and Mg and having a $C_5H_{11}:Br$ ratio ≈ 15) has no effect on the $C_5H_{11}:Br$ ratio, even after heating at $95^\circ C$ for 0.5 h¹⁴. Hence, no extensive redistribution of unsolvated species occurs in hydrocarbons, probably because organomagnesium halides have low solubilities.

Anthracenemagnesium $\cdot 3$ THF reacts in THF with $MgCl_2$ and free anthracene to give¹⁵ the structurally characterized salt $[Mg_2(\mu-Cl)_3(THF)_6]^+[C_{14}H_{10}]^-$.

The reverse of Eq. (a), i.e., redistribution of $RMgX$ reagent, is a convenient route for preparation of diorganomagnesium compounds:



Addition of 1,4-dioxane to an ethereal solution of $RMgX$ reagent precipitates $MgX_2 \cdot 2$ dioxane ($X = \text{halogen, but not F}$), displacing the equilibrium and leaving soluble MgR_2 in solution¹⁶⁻¹⁹. 1,4-Dioxane in a 5-10 % xs is added dropwise to a well-stirred $RMgX$ solution in Et_2O and the mixture left to stir for 12-24 h. The precipitated $MgX_2 \cdot 2$ dioxane is separated by filtration or centrifugation to leave a clear solution of MgR_2 ¹⁶⁻¹⁹. This solution will contain some dioxane and residual halogen; evaporation gives solid product, but removal of all coordinated dioxane requires heating in vacuo at $100^\circ-170^\circ C$ and this is possible for more thermally stable compounds MgR_2 , e.g., when $R = Me, Et, n-Pr, i-Pr, n-Bu, Ph, Me_3CCH_2, Me_3SiCH_2, PhMe_2CCH_2$ but not when $R = i-Bu, t-Bu, n-C_6H_{13}$ ¹⁶⁻¹⁹. Excess dioxane forms $MgR_2 \cdot \text{dioxane}$ ^{18,19}. The procedure is also carried out in THF, e.g., in preparation of $Mg(\text{mesityl})_2$ ¹⁹ and cyclic compounds $Mg(CH_2)_n$ ($n = 4-6$)²¹ probably dimers¹¹:



although the magnesium halide-dioxane adduct is slightly soluble in THF⁵. 1,4-Dioxane will also precipitate MgX_2 from hydrocarbon solution of organomagnesium halides¹⁴.

Addition of pyridine (PY) to some $RMgX$ solutions will precipitate complexes of MgX_2 and form $MgR_2 \cdot 2 PY$ ($R = Et, n-Bu, t-Bu, Ph$)²². Diglyme is also used to

precipitate MgCl_2 from THF solutions of vinylmagnesium chloride¹⁶. Although redistribution of Eq. (a) occurs between $\text{Me}_2\text{Mg}\cdot\text{TMED}$ and $\text{Br}_2\text{Mg}\cdot\text{TMED}$ in benzene, volatile $n\text{-Bu}_2\text{Mg}\cdot\text{TMED}$ can be isolated from $n\text{-BuCl}$ and Mg in hexane-TMED and $\text{Cl}_2\text{Mg}\cdot\text{TMED}$ is precipitated²³.

Pyrolysis of solid RMgBr [$\text{R} = \text{cyclopentadienyl}$ ($200^\circ\text{--}230^\circ\text{C}$)²⁴, indenyl (190°C)²⁵] in vacuo causes redistribution, and MgR_2 is obtained by sublimation ($\text{R} = \text{C}_5\text{H}_5$, 40%²⁴; C_9H_7 , 25%²⁵).

Magnesium ethoxide undergoes redistribution with $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Mg}$ to give $\text{h}^5\text{-C}_5\text{H}_5\text{MgOEt}$ ²⁶; in THF the product is a monomeric THF adduct, but in toluene an unsolvated cubane tetramer is formed.

(W. E. LINDSELL)

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5.4.2. Formation of the Carbon—Mg Bond

5.4.2.3. from Magnesium Halides

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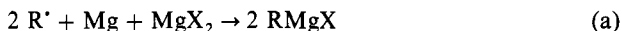
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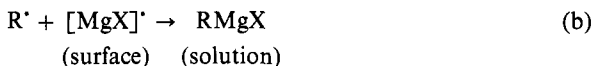
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Stable radicals R^\cdot , where $\{R^\cdot = [Ph_3C]^\cdot{}^2, [Ph(2,2'-C_6H_4C_6H_4)C]^\cdot{}^3\}$ react with a mixture of MgX_2 ($X = Br, I$) and xs Mg metal in ether-benzene at RT (1 week; $R^\cdot = Ph_3C^\cdot$, $X = Br$)² or under reflux [several hours, with addition of $n-Pr_2O$, $R = Ph(C_6H_4C_6H_4)C^\cdot$]³ to give high yields of organomagnesium halide reagents:



More reactive radicals also react by Eq. (a), and this may involve a radical coupling step:



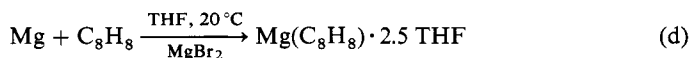
Using catalytic amounts of MgX_2 ($X = Br, I$) the process can be modified to form MgR_2 via $RMgX$ ⁴:



When $R^\cdot = [Ph_3C]^\cdot$, no reaction occurs in the absence of MgX_2 , but reaction (c) occurs in heated Et_2O -benzene (20 h) giving $Mg(CPh_3)_2$ (92%); catalytic MgX_2 may be added or formed in situ by reaction of Mg with a little Ph_3CBr ⁴.

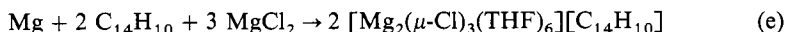
Mixtures of $Mg-MgI_2$ do not react⁵ with Ph_2CH_2 or Ph_3CH in ether-benzene at $60^\circ-65^\circ C$ for 6 h. No reaction takes place between $Ph_2C=CH_2$ and $Mg-MgI_2$ on refluxing in benzene⁶, but styrene in the presence of isoprene reacts with Mg metal activated with $BrCH_2CH_2Br$ (i.e., $MgBr_2$ present) in boiling tetrahydrofuran (THF) giving $Mg(PhCHCH_2CH_2CHPh)$ ⁷. Isoprene reacts with Mg, activated by organic halide, including $BrCH_2CH_2Br$, in THF ($\leq 65^\circ C$) to form adducts, $Mg(C_5H_8)_n$ ($n = 2-8$)⁸. Other conjugated dienes, including butadiene and $Me_2C=CH(CH_2)_2C(CH=CH_2)=CH_2$ (myrcene), react similarly⁸; likewise related preparations of adducts $Mg(diene)_n$ ($n \geq 1$) in THF involve activation procedures that produce some MgX_2 as a side product⁹⁻¹¹ (see also §5.4.2.2.4), so that they may be considered to be related to preparations of this section.

The cyclooctatetraene adduct is formed¹² by catalysis with $MgBr_2$:



Milling anhydr $MgCl_2$ with aromatic materials (e.g., naphthalene, durene) or polymers (e.g., polyethylene) forms stable free radicals that are radical cations supported on $MgCl_2$ ¹³.

Anthracene reacts with Mg metal in THF saturated with $MgCl_2$ to form a blue, ionic dimer containing an anthracene radical anion¹⁴:



Related reactions occur for anthracene with Mg and $MgBr_2$ ¹⁵.

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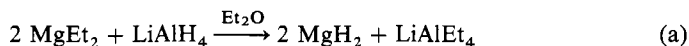
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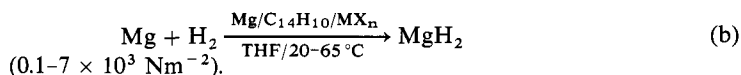
5.4.2.4.1. by Addition to Olefinic or Acetylenic Linkages.

The gray, powdered MgH_2 (see §1.8.3.2) formed by direct interaction of the elements at elevated T and pressures is inactive, showing low reactivity with air or H_2O ^{1,2}. The white MgH_2 formed by pyrolysis³ (ca. 200°C) of MgEt_2 , by metathesis⁴ of MgX_2 [$\text{X} = \text{Br}$ in tetrahydrofuran (THF), $\text{X} = \text{I}$ in Et_2O] with MH ($\text{M} = \text{Na}, \text{K}$) or by reaction of LiAlH_4 with⁵ MgR_2 or ¹ n-BuMgBr in Et_2O is spontaneously inflammable in air and hydrolyzes violently. This active, white MgH_2 is useful in synthesis of $\text{Mg}-\text{C}$ bonds, and its preparation using LiAlH_4 is convenient, e.g.:



The washed, vacuum-dried MgH_2 retains ca. 15% Et_2O ⁵ and may be converted into an active slurry in THF⁶. In preparations by Eq. (a) it is recommended that, if coprecipitation of some hydridoaluminum byproducts (10%) is to be avoided, the $\text{MgEt}_2:\text{LiAlH}_4$ ratio should exceed 2:1^{5,7}; however, in some syntheses a 1:1 ratio is used, with $\text{LiAlH}_2\text{Et}_2$ being the coproduct rather than LiAlEt_4 ^{5,8,9}.

Catalytic hydrogenation of Mg metal in the presence of magnesium-anthracene and a transition-metal halide (CrCl_3 , TiCl_4 , etc.) in THF is a source of active MgH_2 ¹⁰:



(i) Addition to Alkenes. Low-yield additions of MgH_2 to ethene, 2-methylpropene and 1-octene occur in the absence of catalysts at elevated T²:



and the extent of reaction is dependent to some degree on the solvent employed and on the state of MgH_2 . Reaction is negligible in hydrocarbon solvents; it is favored in ethers and a small amount of ether in hydrocarbon promotes reaction². However, ethers also promote side reactions, including further addition of $\text{Mg}(\text{CH}_2\text{CHRR}')_2$ to alkene and solvent cleavage².

Ethene [50–135 atm (5–13.6 × 10³ Nm⁻²)] in Et_2O (100°–110°C) forms MgEt_2 by Eq. (c) in only 4–5% yield when the MgH_2 employed is formed from the elements or by

5.4. Formation of Bonds between Elements

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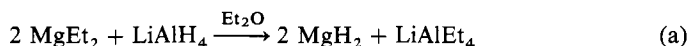
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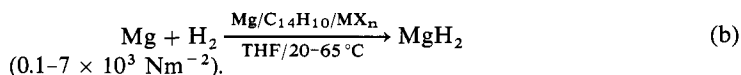
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pyrolysis or hydrogenolysis of MgEt_2 . When the MgH_2 is formed by Eq. (a) the yield of MgEt_2 is 28% under similar conditions². Polyethene is a byproduct, especially after longer reaction times and in diglyme at higher T.

2-Methylpropene in the absence of solvent or in Et_2O gives a complex mixture of alkylmagnesium products in low yield at 100°C and *i*-Bu-Mg-containing species are present in only $\leq 5\%$ yield². At 25°C in a ball mill, MgH_2 and 1-octene in Et_2O give 4% 1-octylmagnesiums². A THF slurry of active MgH_2 does not react with 1-octene after 24 h at RT⁶. In pyridine at 110°C, MgH_2 and 1-octene give 6% 1-octylmagnesiums² (MgH_2 itself reacts with pyridine in 4 h at RT⁹). No addition of MgH_2 to bis-9-fluorenylidene occurs in ethers².

Finely divided MgH_2 reacts with 1-alkenes in coordinating sulfur solvents, including thioethers (e.g., Et_2S), sulfoxides (e.g., Me_2SO , Ph_2SO) and sulfones (e.g., Me_2SO_2 , $\text{i-Pr}_2\text{SO}_2$)¹¹. Thus dialkylmagnesium compounds are formed by Eq. (c) in sulfur solvents at 70–130°C using ethene [ca. 66 atm ($6.7 \times 10^2 \text{ Nm}^{-2}$)], propene [33–66 atm ($3.3\text{--}6.7 \times 10^3 \text{ Nm}^{-2}$)] and 1-pentene and the conversions represent high yields (ca. 80%) based on MgH_2 consumed¹¹.

Equation (c) is catalyzed by additives. In mildly basic ethers (e.g., Et_2O , $\text{i-Pr}_2\text{O}$, $\text{n-Bu}_2\text{O}$) or in aromatic hydrocarbons at 90°–150°C, effective catalysts are Al hydrides or alkyls (e.g., AlH_3 , AlEt_3) dialkylzincs (e.g., ZnEt_2) and boron compounds (e.g., B_2H_6 , BEt_3)¹. Reactions are described for ethene [ca. 66–70 atm ($7 \times 10^3 \text{ Nm}^{-2}$)], catalyst AlH_3], propene [ca. 32 atm ($3.2 \times 10^3 \text{ Nm}^{-2}$)], catalyst AlEt_3] and isobutene [ca. 35 atm ($3.5 \times 10^3 \text{ Nm}^{-2}$)], catalyst ZnEt_2] from which high yields of MgEt_2 , MgPr_2 and $\text{Mg}(\text{Bu-}i)_2$, respectively, are achieved, based on the degree of conversion of MgH_2 ¹². Conversions are low but recovered MgH_2 can be recycled to afford final conversions of up to 80–90%¹². However, ethene [ca. 70 atm ($7 \times 10^3 \text{ Nm}^{-2}$)] is polymerized² by MgH_2 in the presence of BEt_3 in Et_2O at 25°C. Also, in contrast to the above discussion, $[\text{AlMe}_3]_2$ has no effect on the reaction of ethene with MgH_2 in $\text{n-Bu}_2\text{O}$ and, using this catalyst in *n*-heptane, MgH_2 is alkylated by ethene (17%), but the product contains EtMg (46%), n-BuMg (53%) and $\text{C}_6\text{H}_{13}\text{Mg}$ (1%) linkages².

The combined reaction of H_2 and alkene, such as ethene under pressure, on Mg metal at 60°–120°C in the presence of Hg and under photo-activation by irradiation at 2530 Å produces dialkylmagnesiums¹³.

Active MgH_2 , prepared catalytically by using magnesium-anthracene and TiCl_4 or CrCl_3 [Eq. (b)]¹⁰, adds to 1-alkenes in THF. [Eq. (c)] under the influence of transition-metal catalysts. The catalysts initially employed to form MgH_2 are also active for hydromagnesiation^{10,14} but zirconium halides [ZrX_4 (especially ZrI_4), 1 mol %] are best¹⁴ for higher 1-alkenes: ethene is transformed quantitatively to MgEt_2 and $\leq 90\%$ conversions of 1-butene or 1-octene to $\text{Mg}(\text{R-}n)_2$ occur in 1–3 h at 70–100°C with regiospecific addition of metal to the terminal carbon ($>99.7\%$ for 1-octene). No addition of MgH_2 to 1,1- or 1,2-dialkylalkenes takes place under these conditions^{10,14}. Similarly, MgH_2 , formed from MgEt_2 and LiAlH_4 [Eq. (a)], adds to 1-alkenes, but $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (5%) is the best catalyst¹⁵. Again, high yields of $\text{Mg}(\text{R-}n)_2$ are formed (60°C, THF)¹⁵ but lower and variable yields (45–65%)¹⁶ are obtained from 1-octene at RT. Related $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ catalyzed additions to 1-octene at RT occur for HMgX ($\text{X} = \text{Cl}, \text{Br}$) or RMgH ($\text{R} = \text{Me}, \text{Et}, \text{t-Bu}, \text{C}_5\text{H}_5, \text{Ph}$) with MeMgH being the most effective hydrometallating reagent¹⁶; Et_2NMgH also adds under $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ catalysis¹⁷ to 1-alkenes to give high yields of n-RMgNet_2 . An active intermediate in these processes is $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiH}$, and some isomerization to 2-alkene, occurring as a

side-reaction, is the result of β -hydrogen elimination from an insertion product¹⁶, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{Me})\text{CH}_2\text{R}$. Steric influences on $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ -catalyzed additions are important¹⁵: thus, methlenecyclohexane reacts with MgH_2 but cis-hex-2-ene gives a low yield of hydrometallated product, and a tri-substituted alkene, 1-methylcyclo-hexane, shows no reactivity.

Addition of MgH_2 to styrene is best catalyzed by $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ ^{15,18} since TiCl_4 or ZrX_4 catalysts cause extensive oligomerization¹⁸. Reactions take place at RT¹⁵ or in refluxing THF¹⁸ giving $\geq 90\%$ product with metal attached primarily to α -carbon (ratio $\alpha:\beta \geq 9:1$). Under related conditions Et_2NMgH also adds to styrene¹⁷.

The functionalized terminal alkenes, $\text{RR}'\text{N}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ ($n = 1, 2$) and $\text{RO}(\text{CH}_2)_2\text{CH}=\text{CH}_2$, react with MgH_2 and ZrCl_4 (1 mol %) in refluxing THF¹⁹ to form volatile, inner complexes $\text{Mg}[\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{NRR}']_2$ ($\leq 51\%$) and $\text{Mg}[\text{CH}_2(\text{CH}_2)_2\text{OR}]_2$ ($\leq 60\%$). However, $\text{ROCH}_2\text{CH}=\text{CH}_2$ undergoes C—O bond cleavage with MgH_2 under similar conditions¹⁹.

Catalysts for polymerization of ethene and propene^{20,21} contain MgH_2 and TiCl_4 .

The hydrogenation of 1,3-pentadiene by H_2 [64–106 atm ($6.4\text{--}1.06 \times 10^3 \text{ Nm}^{-2}$)] in THF at 186°C is catalyzed selectively by MgH_2 ; in 1.5 h the main products are linear pentenes²². This hydrogenation may involve organomagnesium intermediates. Also, active MgH_2 with a high surface area, formed by hydrogenating Mg and butadiene in the presence of THF, is a useful catalyst for hydrogenating other unsaturated hydrocarbons²³.

1,4-Addition of MgH_2 to isoprene in refluxing THF is catalyzed by $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ giving 70–75% conversion in 24 h to a mixture of MgR_2 compounds ($\text{R} = 2,3\text{- or }3,3\text{-dimethylallyl}$). Poorer conversions are obtained with Zr, Hf or Cr catalysts, and in all cases there is low selectivity between 2,3- and 3,3-dimethylallylmagnesium products¹⁸.

Magnesium hydride reacts with pyridine by addition, but the product contains Mg—N and not Mg—C bonds^{7,9,24}. At 0°–60°C, active MgH_2 forms mainly 1,4-dihydropyridyls, and derivatives of the types $\text{Mg}(\text{NC}_5\text{H}_6)_2$, $\text{HMgN}(\text{C}_5\text{H}_6)$ and $\text{H}_3\text{Mg}_2(\text{NC}_5\text{H}_6)$ are obtained.

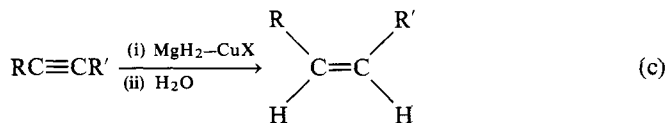
(ii) Addition to Alkynes. In the absence of catalysts, MgH_2 slurry in THF does not add to phenylacetylene at RT over 24 h⁶, and HMgX ($\text{X} = \text{Cl, Br}$) adds to alkynes, but no experimental details are available⁸.

The reactions of propyne and of allene on Mg films are similar²⁵. Some of the hydrocarbon is dehydrogenated at 100°C forming metallated propyne intermediates ($\text{MeC}\equiv\text{CMg}-$); further dehydrogenation at 150°C produces²⁵ Mg_2C_3 . In this dehydrogenation, MgH_2 is also formed, and it hydrogenates other molecules of propyne (or allene) in a two-step mechanism via an organomagnesium intermediate to give propene^{25,26}. The overall process involves self-hydrogenation of propyne or allene. The organomagnesium produced by addition of MgH_2 is stable at 100°C, and reaction with D_2O gives predominantly E-1-[$^2\text{H}_1$]-propene, suggesting cis-addition of the Mg—H bond to the alkyne (propyne or isomerized allene) and the formation of $(\text{ECH}_3\text{CH}=\text{CHMg}-)$ units²⁵; allene also forms allyl- and 2-propenylmagnesium intermediates.

A slurry of MgH_2 in THF in the presence of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (5%) reacts with 4-octyne at RT in 1 h to give, after hydrolysis, cis-oct-4-ene¹⁵; deuteration of the organomagnesium primary product of hydrometallation gives monodeuteriated cis-oct-4-ene (54%) and supports cis addition of MgH_2 to the alkyne. Under similar reaction conditions there is competition between MgH_2 addition and deprotonation in reaction

with the terminal alkyne, 1-octyne; the products of deuterialysis are [$^2\text{H}_1$]-oct-1-ene (50%) and [$^2\text{H}_1$]-oct-1-yne (40%)¹⁵.

The hydrogenation of alkyne to alkene is carried out using an equimolar mixture of MgH_2 (in THF) and CuX ($\text{X} = \text{I}, \text{OBu-t}$)²⁷;



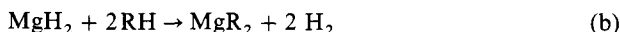
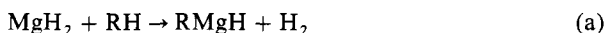
Reaction (d) occurs for terminal alkynes ($\text{R}' = \text{H}$), 1-hexyne, 1-octyne and phenyl acetylene (80–98%), with no further reduction to alkanes²⁷. The internal alkynes, 2-hexyne and diphenylacetylene, give exclusively cis-alkene (80–95%)²⁷. However, the organometallic intermediates of Eq. (d) may contain Cu—C rather than Mg—C bonds.

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5.4.2.4.2. with Acidic Hydrocarbons to Evolve H_2 .

The basicity of the hydride entity in salt-like MgH_2 suggests that metallation of more acidic hydrocarbons should occur:



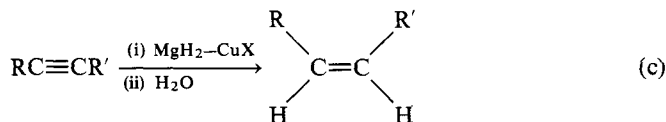
5.4. Formation of Bonds between Elements

5.4.2. Formation of the Carbon—Mg Bond

5.4.2.4. from Magnesium Hydride

with the terminal alkyne, 1-octyne; the products of deuteriolysis are $[^2\text{H}_1]$ -oct-1-ene (50%) and $[^2\text{H}_1]$ -oct-1-yne (40%)¹⁵.

The hydrogenation of alkyne to alkene is carried out using an equimolar mixture of MgH_2 (in THF) and CuX ($\text{X} = \text{I}, \text{OBu-t}$)²⁷;



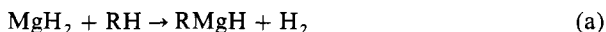
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5.4.2.4.2. with Acidic Hydrocarbons to Evolve H_2 .

The basicity of the hydride entity in salt-like MgH_2 suggests that metallation of more acidic hydrocarbons should occur:



The active, white form of MgH_2 (see §5.4.2.4.1) should be more effective for reactions (a) and (b), but there are few such transformations.

A slurry of active MgH_2 in tetrahydrofuran (THF) does not add to phenylacetylene (see §5.4.2.4.1), and after hydrolysis of a mixture of the reagents, only unreacted $\text{PhC}\equiv\text{CH}$ is recovered¹; however, this is not inconsistent with the formation of some $\text{PhC}\equiv\text{C}-\text{Mg}$ links in the first step, and MgH_2 does metallate phenylacetylene². In the presence of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (5%), MgH_2 in THF reacts with 1-octyne, partially by addition and partially by metallation³; on reaction of the organomagnesium products with D_2O [$^2\text{H}_1$]-oct-1-ene (50%) and [$^2\text{H}_1$]-oct-1-yne (40%) are obtained, and the latter must arise from metallated product (ca. 40%)³. Equimolar mixtures of MgH_2 and CuX ($\text{X} = \text{I}$, $t\text{-BuO}$ give high yields of addition products with 1-octyne, 1-hexyne and phenylacetylene⁴; hydrolysis of these products demonstrates the absence of simple metallated alkynes.

When equimolar cyclopentadiene and MgH_2 are stirred in a THF slurry at RT for a few minutes, a clear solution of $\text{h}^5\text{-C}_5\text{H}_5\text{MgH}$ is formed² [Eq. (a), $\text{R} = \text{C}_5\text{H}_5\text{-h}^5$]. When the solution is concentrated, needle-shaped crystals of $[\text{h}^5\text{-C}_5\text{H}_5(\mu\text{-H})\text{Mg}\cdot\text{THF}]_2$ are obtained. The compound is a dimer in THF and is assigned a structure with four-coordinate Mg and two Mg-H-Mg bridges; it is an active reductant, undergoing single electron transfer with aromatic ketones, triphenylmethyl halides and polynuclear hydrocarbons². Indene² is also metallated by MgH_2 .

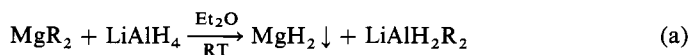
In the context of hydrocarbon metallation, the reaction of MgH_2 with protonic organic molecules including amines⁵, R_2NH , and alcohols or phenols⁶, ROH , to form XMgH ($\text{X} = \text{R}_2\text{N}$, RO) may be mentioned.

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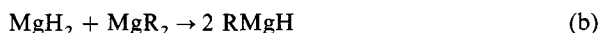
5.4.2.4.3. with Organometallic Compounds.

Active MgH_2 , formed by reaction of MgR_2 ($\text{R} = \text{Et}$ or Ph) with equimolar LiAlH_4 :



reacts with organometallics to produce organomagnesiums (e.g., see ref. 1). It should be noted that MgH_2 obtained by reaction (a) may be contaminated with small amounts of Al hydride species^{2,3}.

(i) Redistribution with Diorganomagnesiums. Addition of MgR_2 in tetrahydrofuran (THF) to a well-stirred slurry of equimolar active MgH_2 in THF, followed by stirring for up to 1 h at RT, affords a quantitative conversion into a clear solution of RMgH ($\text{R} = \text{Me}$, Et , $i\text{-Pr}$, $\text{h}^1\text{-C}_5\text{H}_5$, Ph) by exothermic reaction^{1,4}:



Deuteriated analogues RMgD , are prepared similarly from MgD_2 . The solutions of RMgH in THF are stable at RT for at least 1 day; on evaporation of solvent, solid

5.4. Formation of Bonds between Elements

273

5.4.2. Formation of the Carbon—Mg Bond

5.4.2.4. from Magnesium Hydride

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When equimolar cyclopentadiene and MgH_2 are stirred in a THF slurry at RT for a few minutes, a clear solution of $\text{h}^5\text{-C}_5\text{H}_5\text{MgH}$ is formed² [Eq. (a), $\text{R} = \text{C}_5\text{H}_5\text{-h}^5$]. When the solution is concentrated, needle-shaped crystals of $[\text{h}^5\text{-C}_5\text{H}_5(\mu\text{-H})\text{Mg}\cdot\text{THF}]_2$ are obtained. The compound is a dimer in THF and is assigned a structure with four-coordinate Mg and two Mg-H-Mg bridges; it is an active reductant, undergoing single electron transfer with aromatic ketones, triphenylmethyl halides and polynuclear hydrocarbons². Indene² is also metallated by MgH_2 .

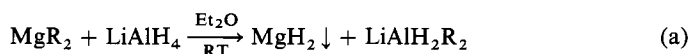
In the context of hydrocarbon metallation, the reaction of MgH_2 with protonic organic molecules including amines⁵, R_2NH , and alcohols or phenols⁶, ROH , to form XMgH ($\text{X} = \text{R}_2\text{N}, \text{RO}$) may be mentioned.

(W. E. LINDELL)

1. E. C. Ashby, J. J. Lin, A. B. Goel, *J. Org. Chem.*, **43**, 1557 (1978).
2. A. B. Goel, E. C. Ashby, *J. Organomet. Chem.*, **214**, C1 (1981).
3. E. C. Ashby, T. Smith, *J. Chem. Soc., Chem. Commun.*, **30** (1978).
4. E. C. Ashby, J. J. Lin, A. B. Goel, *J. Org. Chem.*, **43**, 757 (1978).
5. E. C. Ashby, A. B. Goel, *Inorg. Chem.*, **17**, 1862 (1978).
6. E. C. Ashby, A. B. Goel, *Inorg. Chem.*, **18**, 1306 (1979).

5.4.2.4.3. with Organometallic Compounds.

Active MgH_2 , formed by reaction of MgR_2 ($\text{R} = \text{Et}$ or Ph) with equimolar LiAlH_4 :



reacts with organometallics to produce organomagnesiums (e.g., see ref. 1). It should be noted that MgH_2 obtained by reaction (a) may be contaminated with small amounts of Al hydride species^{2,3}.

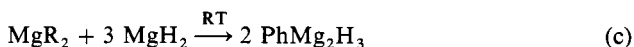
(i) **Redistribution with Diorganomagnesiums.** Addition of MgR_2 in tetrahydrofuran (THF) to a well-stirred slurry of equimolar active MgH_2 in THF, followed by stirring for up to 1 h at RT, affords a quantitative conversion into a clear solution of RMgH ($\text{R} = \text{Me}, \text{Et}, \text{i-Pr}, \text{h}^1\text{-C}_5\text{H}_5, \text{Ph}$) by exothermic reaction^{1,4}:



Deuteriated analogues RMgD , are prepared similarly from MgD_2 . The solutions of RMgH in THF are stable at RT for at least 1 day; on evaporation of solvent, solid

adducts $\text{RMgH} \cdot n \text{ THF}$ are formed and desolvation occurs in vacuo at ca. $100^\circ\text{C}^{1,4}$. In solution, RMgH compounds exhibit varying degrees of association and IR bands in the region $1250\text{--}1300 \text{ cm}^{-1}$, are assignable to bridging Mg--H--Mg linkages¹. Reaction (b) does not occur in Et_2O and, when $\text{R} = \text{Et}$, the reagents may be recovered unchanged in this medium.

When 1:1 MgPh_2 and active MgH_2 are mixed in Et_2O and stirred for $\leq 6 \text{ h}$, a precipitate of PhMg_2H_3 is formed, ($\text{R} = \text{Ph}$):

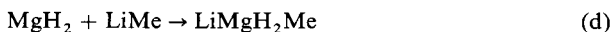


leaving $x \text{ s MgPh}_2$ in solution⁴. Similarly, $\text{PhMgH} \cdot \text{THF}$ disproportionates¹ into MgPh_2 and insoluble PhMg_2H_3 in Et_2O .

Using 3:1 active MgH_2 and MgR_2 in THF, the products RMg_2H_3 ($\text{R} = \text{Ph}, \text{Me}$) are formed via Eq. (c) in high yield^{1,4}. Solid PhMg_2H_3 (containing residual ether) may be obtained by evaporating the colorless solution in THF and washing with Et_2O , in which it is insoluble; although PhMg_2H_3 is soluble in THF, it slowly cleaves THF at RT and at reflux to $\text{PhMg}_2(\text{O}i\text{Bu})_3$ is obtained⁴. The methyl derivative, MeMg_2H_3 , forms a clear solution in THF, but on removal of solvent under vacuum it disproportionates¹ into MeMgH and MgH_2 . It is not possible to prepare $i\text{-PrMg}_2\text{H}_3$ by Eq. (c) in THF; only $i\text{-PrMgH}$ is formed by Eq. (b) in the presence of $x \text{ s MgH}_2$ ¹. Also, a 1:3 mixture of $\text{MgH}_2\text{:MgPh}_2$ in THF does not produce $\text{Ph}_3\text{Mg}_2\text{H}^1$.

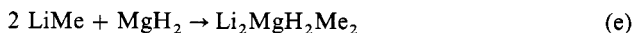
(ii) Reaction with Organolithiums. Organometallic ate complexes $\text{Li}_n\text{MgH}_2\text{Me}_n$ ($n = 1, 2$), are synthesized⁵ by combination of active MgH_2 with LiMe .

Reaction of 1:1 LiMe with MgH_2 in THF (1 h, RT) gives a clear solution containing a product of empirical formula⁵ $\text{LiMgH}_2\text{Me}^5$:

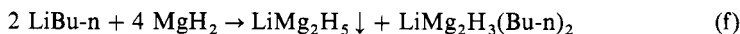


which has an associated structure and slowly cleaves THF at RT.

A 2:1 ratio of LiMe:MgH_2 in THF at RT produces a colorless solution containing the ate complex of empirical formula⁵ $\text{Li}_2\text{MgH}_2\text{Me}_2$:



Addition to $n\text{-LiBu}$ in hexane at 0°C of 2 equiv of MgH_2 slurry in THF followed by warming to RT and stirring for 2 h gives a precipitate of LiMg_2H_5 . The filtrate from this reaction contains a complex organometallic with empirical formula⁵ $\text{LiMg}_2\text{H}_3(\text{Bu-}n)_2$:



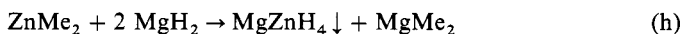
Reaction of LiAlPh_4 with equimolar active MgH_2 by stirring at RT in THF forms a clear solution with PhMgH as a product⁴:



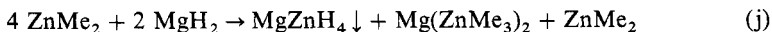
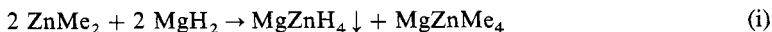
By addition of benzene to this THF solution, the PhMgH is precipitated, but this is contaminated with a small amount⁴ of LiAlHPh_3 .

(iii) Reaction with Organozincs. Reactions in THF between ZnMe_2 and active MgH_2 in various stoichiometries form insoluble MgZnH_4 and a solution containing a methylmagnesium product⁶.

Dropwise addition of 1:2 ZnMe_2 in THF to a well-stirred slurry of MgH_2 in THF and continued stirring at RT for 4 h forms MgMe_2 quantitatively⁶:



The solvated product is precipitated as a $\text{MgZnH}_4 \cdot 2 \text{ THF}$. Similar reaction between 1:1 or 2:1 ZnMe_2 and MgH_2 produce ate complexes⁶:



These have the stoichiometry shown, but spectral evidence shows that they exist in equilibria with the binary dimethylmetal derivatives⁷. The ate complex MgZnMe_4 , itself, prepared from 1:1 MgMe_2 and ZnMe_2 , reacts with 2 equiv active MgH_2 in THF (5 h, RT) to precipitate $\text{MgZnH}_4 \cdot 2 \text{ THF}$ and form MgMe_2 ⁶:



(W. E. LINDSELL)

1. E. C. Ashby, A. B. Goel, *J. Org. Chem.*, **42**, 3480 (1977).
2. E. C. Ashby, R. G. Beach, *Inorg. Chem.*, **9**, 2300 (1970).
3. A. J. De Koning, P. H. M. Budzelaar, B. G. K. Van Aarssen, J. Boersma, G. J. M. Van der Kerk, *J. Organomet. Chem.*, **217**, C1 (1981).
4. E. C. Ashby, A. B. Goel, *Inorg. Chem.*, **16**, 1441 (1977).
5. E. C. Ashby, A. B. Goel, *Inorg. Chem.*, **17**, 322 (1978).
6. A. B. Goel, S. Goel, E. C. Ashby, *Inorg. Chem.*, **18**, 1433 (1979).
7. E. C. Ashby, K. C. Nainan, H. S. Prasad, *Inorg. Chem.*, **16**, 348 (1977).

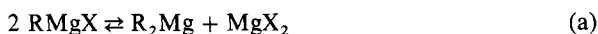
5.4.2.5. from Other Organomagnesium Derivatives

Sections 5.4.2.5.1 through 5.4.2.5.3 describe reactions of organomagnesiums that yield new carbon—Mg bonds and hence are syntheses of new organomagnesiums. Organomagnesiums are sometimes also interconverted by isomerization. Because in type these isomerizations fit into §5.4.2.5.1 and 5.4.2.5.3, however, isomerization is not included as a separate category.

Interest in reactions described in §5.4.2.5.1 through 5.4.2.5.3 is often less with the organomagnesium produced than with the reaction that produces it or with some product available from its subsequent reaction. The organomagnesiums are not isolated and characterized, and only rarely are their solutions studied spectrally. Consequently, their structures and yields must be inferred from the products obtained from quenching their solutions. For that reason, the quenching reagent is often indicated (in parentheses), and the yields cited are often lower limits. When the quenching agent is H_2O , however, the reported yields may be too high, because some replacement of Mg by hydrogen atoms may occur by attack on solvent or some other reagent prior to hydrolysis.

Care in excluding O_2 and H_2O , of course, is necessary in all operations involving organomagnesiums. Other than that precaution, no unusual procedure is involved in the reactions described in §5.4.2.5.1 through 5.4.2.5.3.

Throughout these sections, the organomagnesium-halide reagent is represented by RMgX . Because of the equilibrium:



however, the reagent is actually a mixture of several species.

(H. G. RICHEY, JR.)

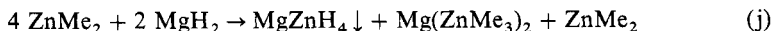
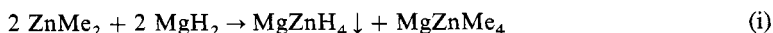
5.4. Formation of Bonds between Elements

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5.4.2. Formation of the Carbon—Mg Bond

5.4.2.5. from Other Organomagnesium Derivatives

The solvated product is precipitated as a $\text{MgZnH}_4 \cdot 2 \text{ THF}$. Similar reaction between 1:1 or 2:1 ZnMe_2 and MgH_2 produce ate complexes⁶:



These have the stoichiometry shown, but spectral evidence shows that they exist in equilibria with the binary dimethylmetal derivatives⁷. The ate complex MgZnMe_4 , itself, prepared from 1:1 MgMe_2 and ZnMe_2 , reacts with 2 equiv active MgH_2 in THF (5 h, RT) to precipitate $\text{MgZnH}_4 \cdot 2 \text{ THF}$ and form MgMe_2 ⁶:



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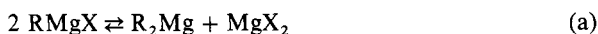
5.4.2.5. from Other Organomagnesium Derivatives

Sections 5.4.2.5.1 through 5.4.2.5.3 describe reactions of organomagnesiums that yield new carbon—Mg bonds and hence are syntheses of new organomagnesiums. Organomagnesiums are sometimes also interconverted by isomerization. Because in type these isomerizations fit into §5.4.2.5.1 and 5.4.2.5.3, however, isomerization is not included as a separate category.

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Throughout these sections, the organomagnesium-halide reagent is represented by RMgX . Because of the equilibrium:

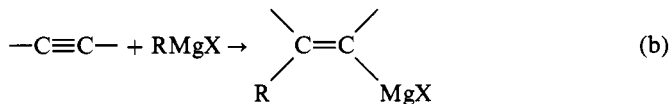
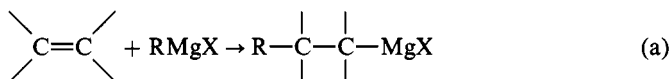


however, the reagent is actually a mixture of several species.

(H. G. RICHEY, JR.)

5.4.2.5.1. by Addition to Alkene or Alkyne Functions: Carbomagnesiation.

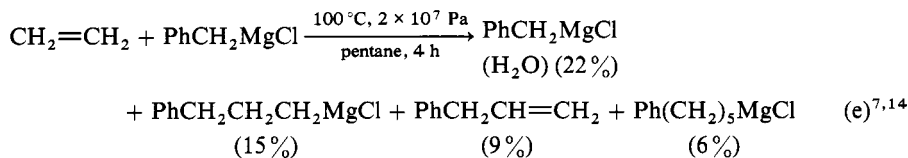
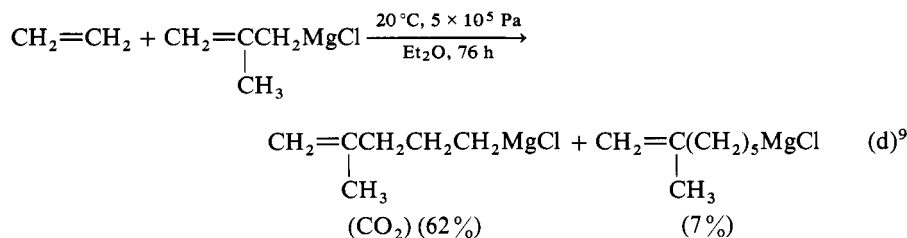
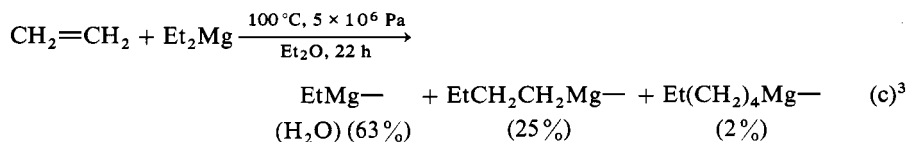
Addition of an organomagnesium to a compound containing a carbon—carbon multiple bond provides a method of forming a new carbon—carbon bond and producing a new organomagnesium available for additional reactions¹:

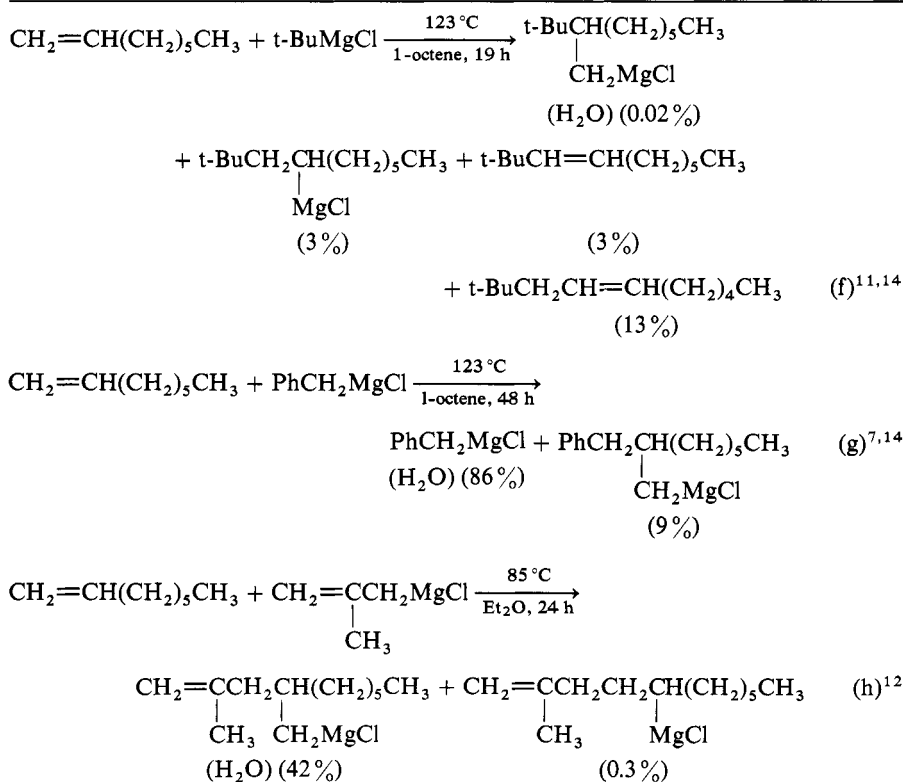


Excluded from this section are the often facile additions, such as to α,β -unsaturated ketones or nitriles, that furnish products in which Mg is associated more with a heteroatom than with a carbon. Also excluded are reactions in which an organomagnesium alone, or in conjunction with other metallic components, catalyzes polymerization of alkenes.

Addition of organomagnesiums to isolated (nonconjugated) alkene and alkyne functions unfortunately is a marginal rather than a general reaction. Although authenticated examples of such additions are known, they involve an unusually reactive organomagnesium, an unusually reactive alkene, elevated T or some special catalytic feature. For that reason, such reactions do not provide a general way to new organomagnesiums, even though the scope, feasibility and mechanisms of such reactions attract interest.

As illustrated below, additions to ethylene and monoalkylethylenes ($\text{RCH}=\text{CH}_2$) occur when vigorous conditions and the more reactive organomagnesium compounds are used²⁻¹³:

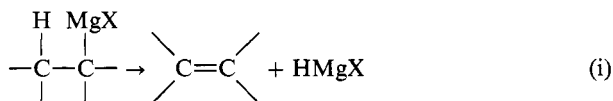




Generalizations applying to the above types of additions are:

1. Additions of allylic organomagnesium halide reagents to simple alkenes are first order in each reactant¹³.
2. Additions to ethylene are easier than to monoalkylethylenes, $\text{RCH}=\text{CH}_2$. Significant addition is not observed with more substituted acyclic alkenes (e.g., with 1,1- or 1,2-dialkylethylenes).
3. In these additions, allylic organomagnesiums are the most reactive. Only with these are normal conditions (Et_2O at $\leq 35^\circ\text{C}$) sometimes sufficient for successful additions. Effects of one or two methyl substituents on the allylic system are small but vary in a manner that suggests the interplay of several factors¹³. Tertiary organomagnesiums are next in reactivity, followed by secondary and benzyl. Primary, methyl and phenyl organomagnesiums are lower in reactivity. Primary organomagnesiums add to ethylene but not to monoalkylethylenes. Additions of methyl or phenyl organomagnesiums are unknown.
4. An addition product can react with more alkene. Such oligomerization is more difficult to avoid, of course, when reactivity of the organomagnesiums produced by addition equals or exceeds that of the initial organomagnesium. In reactions such as Eq. (c), e.g., of primary organomagnesiums with ethylene to produce new, primary organomagnesiums, multiple addition is significant. A reaction similar to that in Eq. (c) but in hexane or heptane produces oligomers, C_{10} and larger, and a little

- polyethylene²; when more vigorous conditions are used, primary organomagnesiums and ethylene produce more polyethylene³. By contrast, multiple additions can be minimal when, as in Eqs. (d) and (e), e.g., more reactive organomagnesiums are used.
5. Yields of new organomagnesiums often are poor. Because additions are usually slow, even when severe conditions are used, poor yields may result from insufficient time for reaction. Low yields also arise, however, from side reactions. Note, in Eq. (f), e.g., the isolation of alkenes that form before quenching by elimination of an Mg hydride:

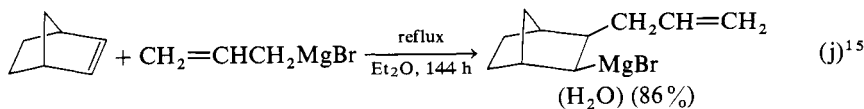


At the high T needed for addition, such elimination from t-butylmagnesium chloride (to form isobutene) and from other organomagnesiums with β -hydrogens can compete with their additions to alkenes.

6. Orientation of addition to monoalkylethylenes ($\text{RCH}=\text{CH}_2$) depends on the nature of the organomagnesium. In Eq. (f), e.g., the product results from attachment of the t-butyl group to the terminal carbon of the double bond. In Eq. (h), however, attachment of 2-methyl-2-propenyl is to the internal carbon. The regioselectivity correlates with the sum of σ^* values for R, R' and R'' in $\text{RR}'\text{R}''\text{MgCl}$, the amount of terminal attachment of the alkyl group increasing as σ^* becomes more negative¹².
7. Even though the solubilities of organomagnesiums in hydrocarbons are often low, additions are faster in hydrocarbons (alkanes and benzene) than in Et_2O . Additions are slower, however, in tetrahydrofuran (THF), a solvent more effective than Et_2O in coordinating with organomagnesiums.

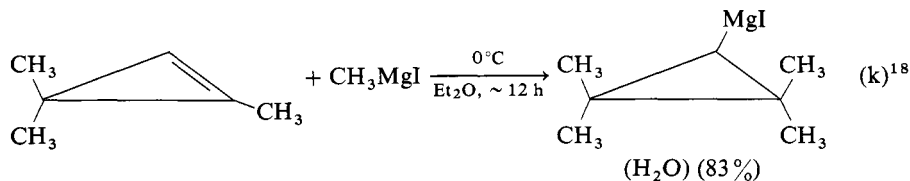
In the remainder of this section, special features are considered—structural factors in the unsaturated substrate and catalytic additives—that can facilitate additions of organomagnesiums to carbon-carbon multiple bonds.

(i) **Strain in the Unsaturated Substrate.** Although addition to acyclic dialkylethylenes is not ordinarily seen, addition is noted to strained cyclic alkenes. A number of allylic organomagnesium-halide reagents add in good yield to bicyclo[2.2.1]-hept-2-ene^{7,9,10,13,15-17}:

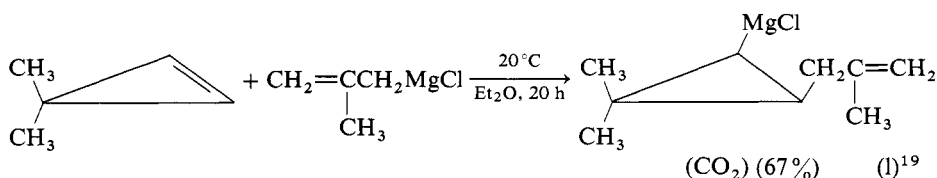


An 11% yield of an addition product is obtained from benzylmagnesium chloride (95°C, no additional solvent, 40 h)^{7,14}.

Additions to cyclopropenes are more facile, because of their large ring strain. Organomagnesium-halide reagents add to cyclopropenes¹⁸⁻²⁹; e.g., mild conditions suffice for addition of a methylmagnesium-halide reagent in:

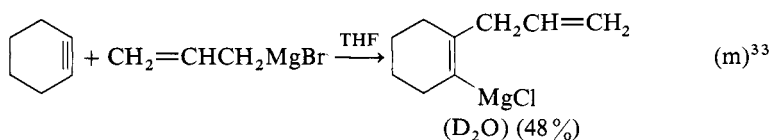


Other organomagnesium-halide reagents added include ethyl, butyl, phenyl and vinyl. The products obtained by quenching are *cis*, e.g.:

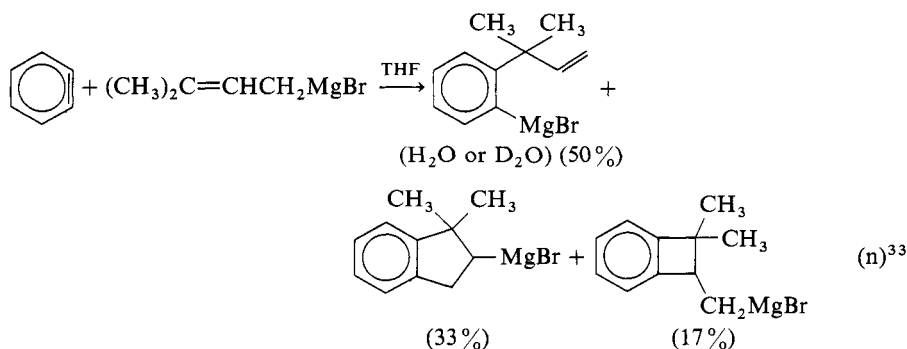


Because cyclopropylmagnesium-halide reagents are configurationally stable^{30–32}, no isomerization occurs subsequent to addition and the R and Mg of the organomagnesium add in a *syn* fashion. Relative rates of addition to a cyclopropene of R_2Mg , where R is methyl, ethyl, isopropyl or *t*-butyl, are 1, 10, 32 and 8, values that are similar²⁹.

Organomagnesiums add to allenes⁶, but additions to simple alkynes are not yet demonstrated. Some products, however, are ascribed to the addition of allylic reagents to the highly strained, short-lived cyclohexyne formed in situ by the reaction of 1,2-dibromocyclohexene and Mg metal³³:

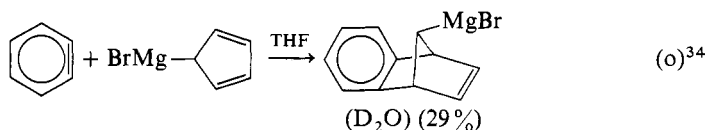


A similar addition product is noted in reactions with benzene, generated in situ³³:

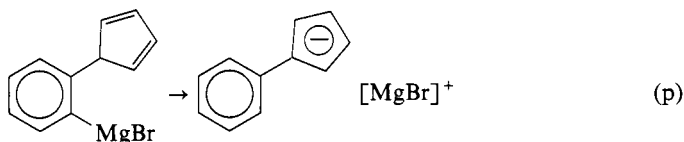


As is found in other additions in this section, and many other reactions of allylic organomagnesiums, formation of the new C—C bond is predominantly at the more substituted carbon of the unsymmetrical allylic organometallic. The product of simple addition also is accompanied by cyclopentane and cyclobutane products arising formally from 3 + 2 and 2 + 2 cycloadditions of the allylic system and benzyne.

Cyclopentadienylmagnesium-halide reagents in THF react with benzyne to give only products of 2 + 3 cycloadditions³⁴:



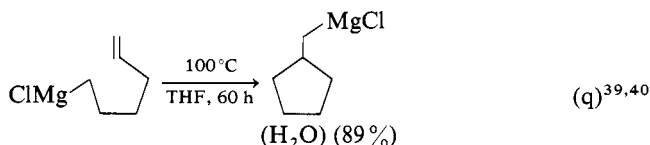
As in Eq. (o), Mg in the products is anti to the aromatic ring. A product resulting from simple addition (followed by metallation of the acidic cyclopentadiene ring) also is formed, however, when 2 equiv of hexamethylphosphoramide (HMPA) are present³⁵:



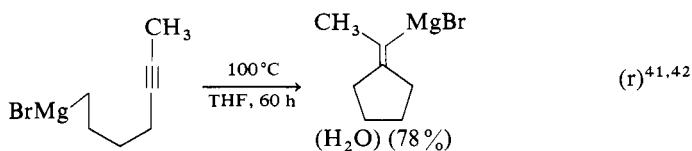
Because HMPA would increase the ionic character of the cyclopentadienyl reagent, the cycloaddition product results from concerted cycloaddition of a σ -bonded cyclopentadienylmagnesium to the benzene³⁵.

(ii) An Intramolecular Organomagnesium Function in the Unsaturated Substrate. Intramolecular additions of organomagnesium functions to alkene and alkyne functions can be easier than comparable intermolecular additions^{36,37}. As in Eqs. (q)–(u), these reactions form cyclic organomagnesium compounds.

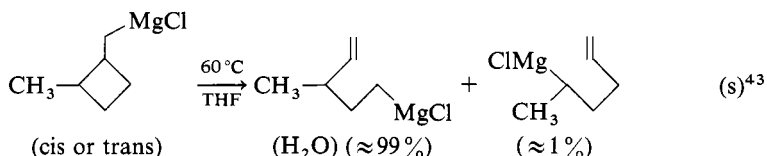
Note that in Eq. (q), e.g., even a primary organomagnesium function adds to a monoalkylethylene:



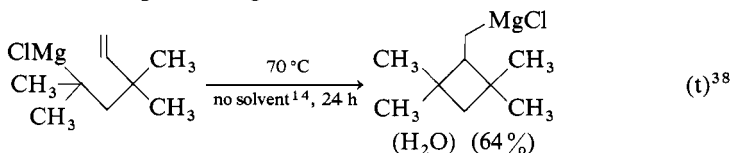
As illustrated in Eq. (r), additions occur to alkyne functions, even though comparable intramolecular additions are not known:



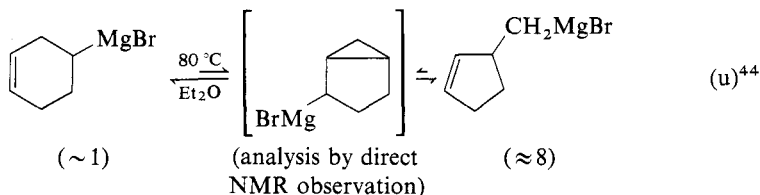
Such reactions are reversible, of course, but in the absence of special factors, the equilibrium ordinarily greatly favors the cyclic isomers when five- or six-membered but no three- or four-membered rings are involved:



This preference can be reversed by appropriate substitution, however, as in Eq. (t). The methyl groups in this system favor cyclization both because a tertiary organomagnesium function is converted to a more stable primary one and because of the usual effects of alkyl substituents in stabilizing small rings:



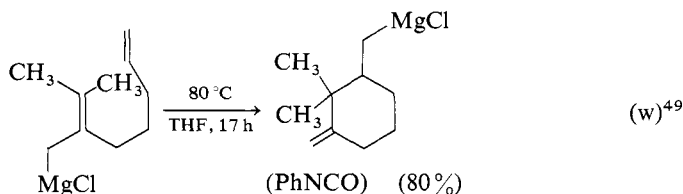
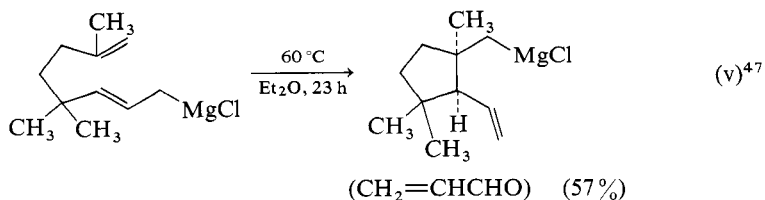
Cyclization to an organomagnesium compound sufficiently less stable to be present only in small amounts at equilibrium, however, can lead to rearrangement. The organo-magnesium-halide reagent either at the left or at the right in Eq. (u) forms a ca. 1:8 mixture of these reagents, by cyclization-cleavage.



Generalizations can be made about these reactions:

1. Cyclization ordinarily produces exclusively the reagent with the smaller of the two possible rings. In Eq. (q), e.g., a cyclopentylmethyl rather than a cyclohexyl reagent is formed.
2. In ring closures to rings of different sizes, rates decrease in the order of $C_3 > C_5 > C_4 > C_6$. Alkyl substituents at either end of the double bond decrease the cyclization rate. For systems with different numbers of methyl substituents at the α -carbon, the unusual reactivity order $1^\circ < 2^\circ > 3^\circ$ is observed.
3. In ring cleavages, relative reactivities of organomagnesium compounds having α -cycloalkyl groups follow the order $C_3 > C_4 \gg C_5, C_6$.
4. The reactions generally are first-order, more rapid in Et_2O than in THF and speeded by addition of hydrocarbons to ether solutions.

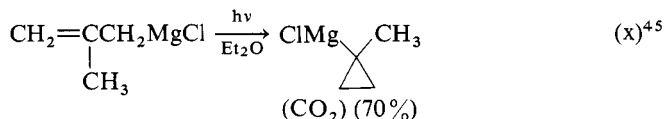
Intramolecular additions involving allylic-organometallic functions can be facile⁴⁵⁻⁵⁴:



Even formation of seven-membered rings occurs⁴⁹. Cyclizations of alkenes containing allylic-organomagnesium functions are key steps in several efficient syntheses of natural products^{47,48,50-52,54}. Formation of the smaller possible ring occurs, as observed with other intramolecular-organomagnesium additions. As in other additions, intermolecular or intramolecular, of unsymmetrical allylic organomagnesiums, attachment is to the more alkylated allylic carbon, e.g., Eq. (w). The cis-trans stereochemistry of ring substituents, e.g., Eq. (v) is rationalized successfully by regarding these cyclizations as

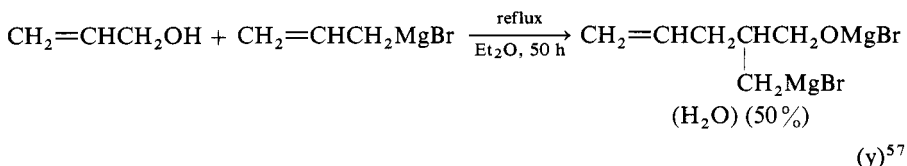
"Mg-ene reactions" in which transfer of Mg from the less-substituted allylic carbon to a carbon of the alkene function occurs simultaneously with formation of the carbon-carbon bond.

The endothermic isomerization of allylic to cyclopropyl reagents is achieved photochemically⁴⁵:

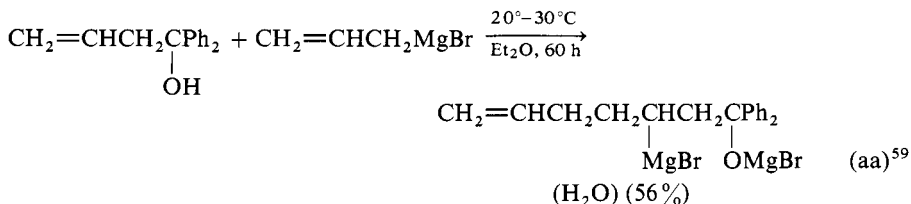
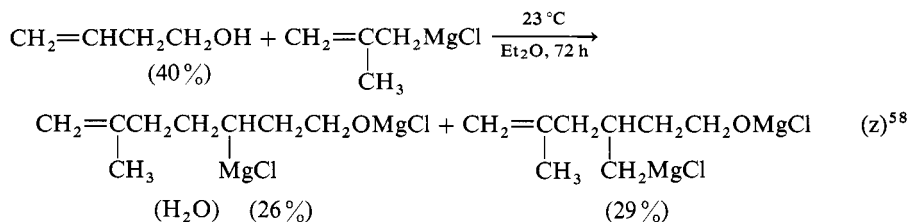


(iii) A Hydroxyl or Similar Group in the Unsaturated Substrate. Additions are readier when the unsaturated substrate contains a suitably placed hydroxyl function⁵⁶. Such additions occur to both alkenols⁵⁷⁻⁶⁸ and alkynols^{60,61,69-72}. Excess organomagnesium must be used, because 1 mol reacts rapidly to metallate the hydroxyl group. The metallated hydroxyl group assists addition. Although structures of the addition products in the examples show different Mg's bonded to the oxygen and carbon, the same Mg may link these atoms into a ring.

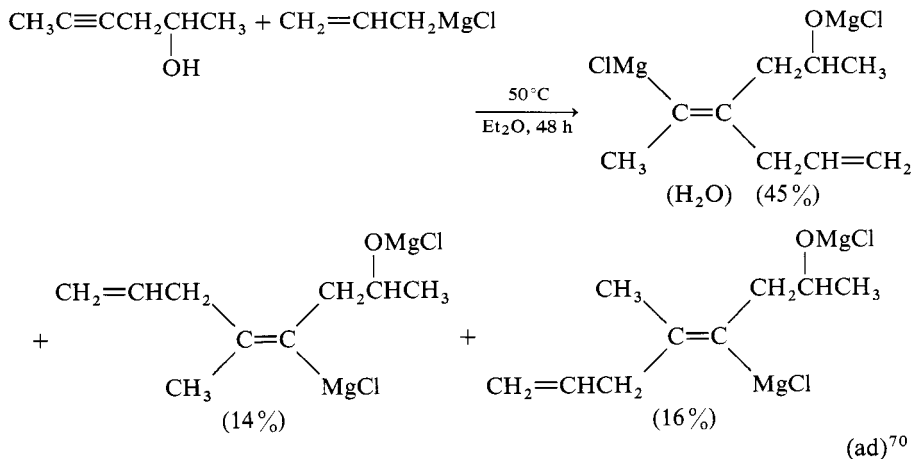
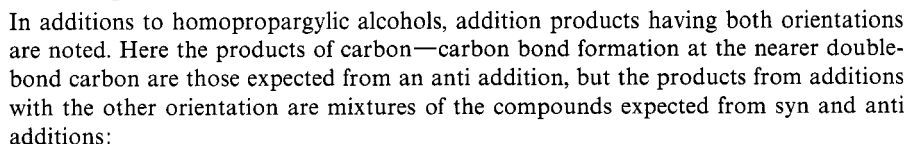
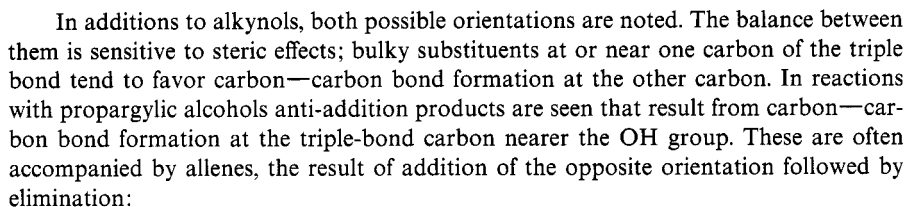
In reactions with allylic alcohols the new carbon—carbon bond generally forms at the double-bond carbon nearer to the hydroxyl group, e.g.:



By contrast, in reactions with homoallylic alcohols the new carbon—carbon bond formation at the more remote double-bond carbon becomes the exclusive process if the groups R in H₂C=CHCH₂CR₂OH are larger than hydrogen:



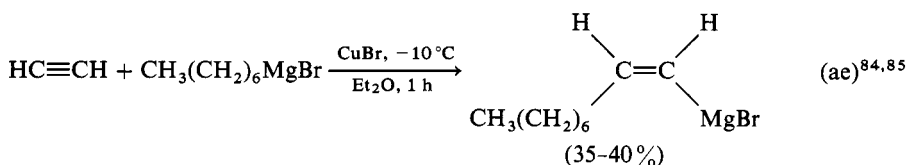
In cyclic systems, in which the stereochemical relationship is evident, both the organic group and the Mg are attached to the face of the double bond nearer the OH group. Cyclization subsequent to addition can occur if the addition product has suitably placed alkene and organomagnesium functions and cyclization leads to a more stable product:



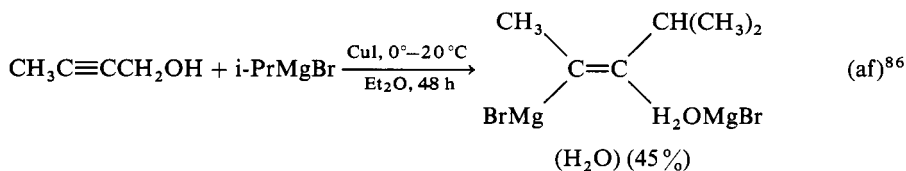
Assistance generally is less favorable when the relationship between the double or triple bond and the OH group is more distant than allylic or homoallylic. Assisted additions are also observed to allenols.⁷⁴ Assistance is also observed by other groups, including primary and tertiary amino^{69,75–77}, alkoxy^{59,78} and phenolic hydroxyl⁷⁹, and in unsaturated substrates containing more than one assisting functional group^{69,80,81}.

(iv) Catalysis by Transition-Metal Compounds. Among the various, often complicated reactions of organomagnesiums catalyzed by transition-metal compounds are several that result in addition of organomagnesiums to an alkene or alkyne⁸². Excluded from consideration are many reactions in which most products do not contain C—Mg bonds. A competing transition-metal-catalyzed reaction of organomagnesiums and alkenes is described in §5.4.2.5.3.

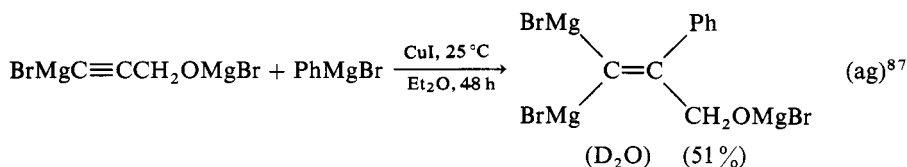
Additions of organomagnesium-halide reagents to alkynes are, e.g., catalyzed by Cu(I) compounds in small amounts (a few mol % of the amount of organomagnesium-halide reagent)⁸³.



Although acetylene usually is metallated by organomagnesium-halide reagents (see §5.4.2.5.2), the presence of a CuBr catalyst causes addition, exclusively syn^{84,85}. In the presence of a CuI catalytic, most organomagnesium-halide reagents (not just allylic) add under mild conditions to propargylic alcohols⁸⁶. The products result from addition that is anti and has the orientation found in, e.g.:

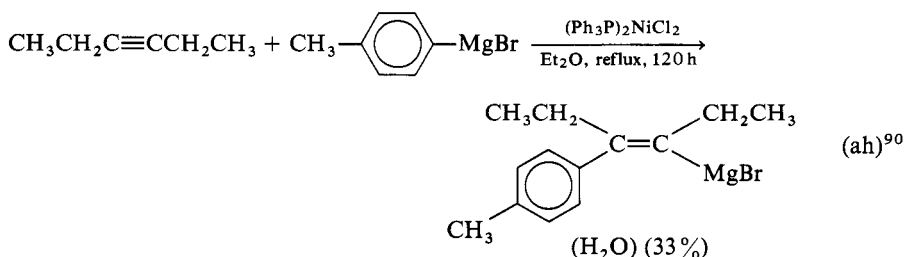


Addition also occurs to dimetalated propargyl alcohols to form di(halomagneso) products:



Addition also takes place to allenols^{88,89}.

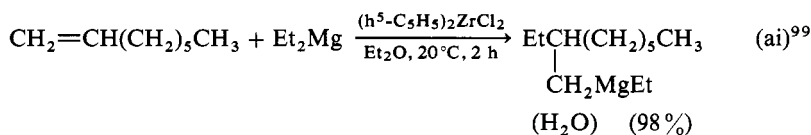
Also, (Ph₃P)₂NiCl₂ catalyzes the syn addition of organomagnesium halides to unsubstituted alkynes:



When organomagnesium-halide reagents (e.g., ethyl, isopropyl) having β hydrogens are used, reduction products resulting from formal addition of a HMgX species are also formed; e.g., NiCl₂ catalyzes addition of arylmagnesium bromides to ethylene⁹¹ and propylene⁹², though the addition products are accompanied by products that result from the alkene–organomagnesium-halide reagent equilibration discussed in §5.4.2.5.3. Alkylmagnesium-halide reagents in the presence of NiCl₂ give no addition products but only products of the alkene–organomagnesium-halide reagent equilibration^{91,92}. In these Cu- and Ni-catalyzed reactions, addition must be of some organocopper or organonickel followed by replacement of the metal in the addition product by Mg.

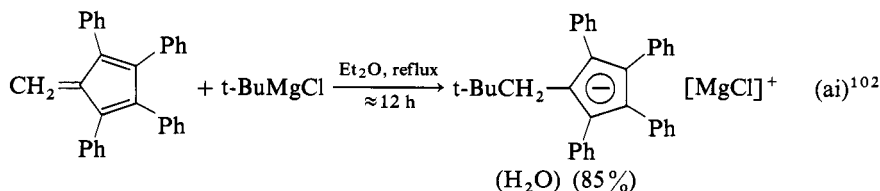
In the presence of large (not catalytic) amounts of various halogen-containing compounds of transition metals, including Rh, and Co, methylmagnesium-halide reagents and PhC≡CPh form (after hydrolysis) product mixtures that include an addition product, PhCH=C(CH₃)Ph^{93–97}. The extent to which precursors of this product contain bonds from carbon to Mg rather than to another metal is not certain, however.

The most studied and general additions to alkenes use (h⁵-C₅H₅)₂ZrCl₂ as catalyst^{98–101}; e.g., Et₂Mg adds to terminal alkenes:

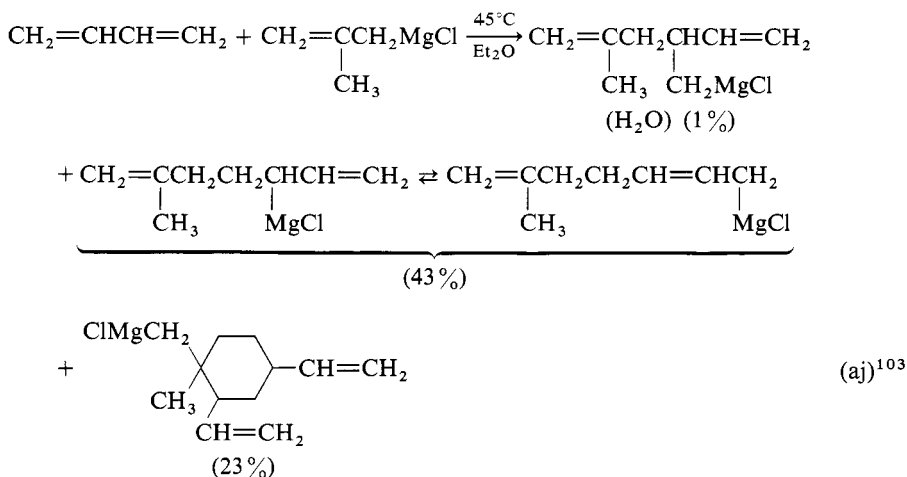


Addition is slower to terminal alkenes that have electron-withdrawing substituents in the allylic position and does not occur with disubstituted alkenes except to bicyclo-[2.2.1]hept-2-enes. Additions are more rapid with Et₂Mg than with EtMgX where X is a halogen, NR₂, or OR. Similar reactions with dipropylmagnesium or dibutylmagnesium lead to substantial formation of alkenes (by dehydromagnesiation of the addition products) and of higher mol wt products.

(v) Conjugated and Electron-Withdrawing Substituents in the Unsaturated Substrate. Additions are more rapid to conjugated than to isolated alkene or alkyne functions. Additions are observed to fulvenes, reactions favored by the stability of the cyclopentadienylmagnesiums that are generated:

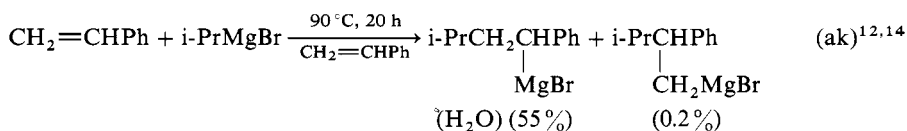


Additions are also observed to conjugated dienes^{6,7,9,103}:



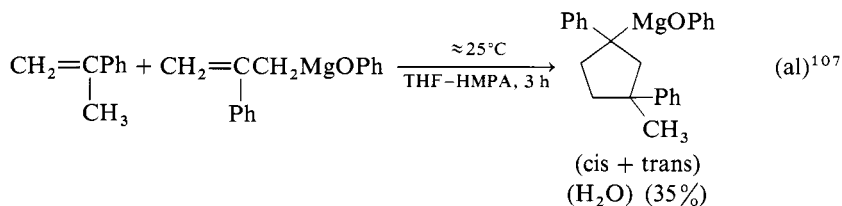
Note the presence of a product owing to further addition of the initial addition product to another butadiene, followed by cyclization; this product of further reaction occurs even when, as in this example, a 1:1 stoichiometry is used. Additions are also observed to conjugated enynes¹⁰⁴.

Addition also occurs to the alkene function of styrene^{9,10,12,13,105}:

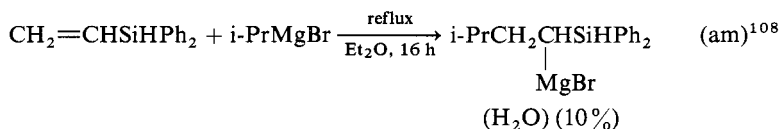


Additions of allylic reagents to styrene initially produce a lot of addition products (primary rather than secondary conjugated organomagnesiums) that result from the other orientation of addition. These additions are reversible, however, and ultimately the more stable conjugated products (and products of their intramolecular cyclization) predominate¹³.

An allylic magnesium phenoxide adds to several aryl-substituted alkenes to give cycloaddition products, although these may be formed in a stepwise rather than a concerted fashion^{106,107}:

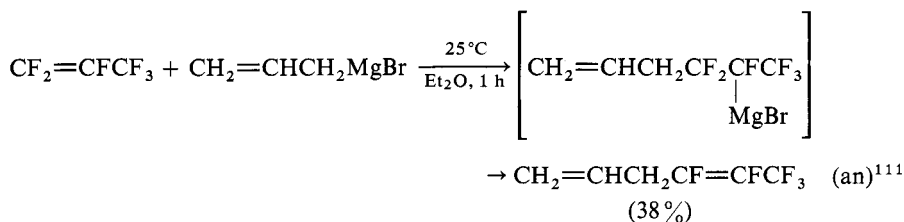


Organomagnesium halide reagents also add to vinylsilanes, a reflection perhaps of some ability of Si to reduce negative charge conjugatively on an adjoining carbon¹⁰⁸⁻¹¹⁰:



Reactions are more facile when the Si is substituted with one or more alkoxy groups^{108,109}.

Addition of organomagnesiums is favored by strongly electron-withdrawing substituents on an alkene, even when the substituents are not capable of conjugating. Allylic reagents react readily with polyfluorinated alkenes, e.g.¹¹¹⁻¹¹⁶:



The reactions proceed by addition of the organomagnesium-halide reagents but are followed by rapid eliminations so that only alkenes are obtained as products.

Additions to conjugated systems are further facilitated by some of the features discussed previously; e.g., additions to dienes^{117,118} and enynes¹¹⁹ in the presence of transition-metal catalysts and additions to enynes¹⁰⁴ containing a suitably placed intramolecular function such as hydroxyl. Although uncatalyzed intermolecular additions to alkynylsilanes are not yet demonstrated, additions are seen in the presence of a transition-metal catalysts¹²⁰ and intramolecular additions to alkynylsilane functions by suitably placed internal organomagnesium-halide functions are facile¹²¹.

(H. G. RICHEY, JR.)

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119. L. M. Zubritskii, T. N. Fomina, Kh. V. Bal'yan, *J. Org. Chem. USSR (Engl. Transl.)*, **17**, 63 (1981); **18**, 1209 (1982).
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121. S. Fujikura, M. Inoue, K. Utimoto, H. Nozaki, *Tetrahedron Lett.*, 1992 (1984).

5.4.2.5.2. by Metallation of Acidic Hydrocarbons.

Metal-hydrogen exchange between organomagnesiums and hydrocarbons can be used to prepare new organomagnesiums¹:

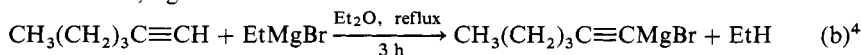


The equilibrium lies to the right when RH is more acidic than R'H, and organomagnesiums can be prepared in this fashion; however, the method is limited by kinetic factors. Even at elevated T, rates are sufficiently rapid to be useful only for metallations of compounds with acidic hydrogens.

From preparation of different classes of organomagnesium compounds by metallation are excluded metallations, often relatively facile, of hydrogens on carbons next to groups such as carbonyl or cyano that produce organomagnesiums in which the metal is associated more with a heteroatom than with carbon.

(i) 1-Alkynylmagnesiums^{2,3}. Metallation of terminal alkynes is the metal-halogen exchange used most to prepare new organomagnesiums. The hydrogen attached to a triply bonded carbon is acidic.

Metallation is effected by adding an alkyne to an Et₂O solution of organomagnesium-halide reagent, most often ethylmagnesium bromide, and then heating the solution at reflux, e.g.:



5.4. Formation of Bonds between Elements

5.4.2. Formation of the Carbon—Mg Bond

5.4.2.5. from Other Organomagnesium Derivatives

95. N. Garty, M. Michman, *J. Organomet. Chem.*, **36**, 391 (1972).
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5.4.2.5.2. by Metallation of Acidic Hydrocarbons.

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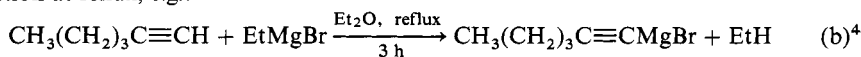


The equilibrium lies to the right when RH is more acidic than R'H, and organomagnesiums can be prepared in this fashion; however, the method is limited by kinetic factors. Even at elevated T, rates are sufficiently rapid to be useful only for metallations of compounds with acidic hydrogens.

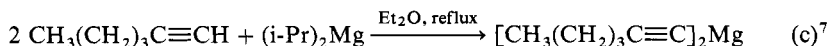
From preparation of different classes of organomagnesium compounds by metallation are excluded metallations, often relatively facile, of hydrogens on carbons next to groups such as carbonyl or cyano that produce organomagnesiums in which the metal is associated more with a heteroatom than with carbon.

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Metallation is effected by adding an alkyne to an Et₂O solution of organomagnesium-halide reagent, most often ethylmagnesium bromide, and then heating the solution at reflux, e.g.:

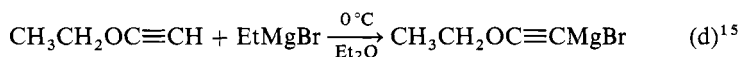


Progress of a metallation can be monitored by observing gas (ethane) evolution. For simple alkynes, only a few hours at reflux are necessary for complete metallation⁵. Substituted terminal alkynes, including conjugated ones, are metallated this way⁶. Similar reactions with dialkylmagnesiums can produce di(1-alkynyl)magnesiums:



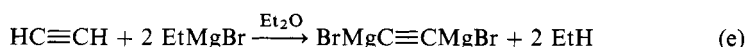
Generalizations about these metallations are:

1. The reactions are first-order in alkyne and first order in organomagnesium^{8–11}.
2. The effect on metallation rate of the particular halogen (X) in RMgX is not large¹². Metallation by the first alkyl group of a dialkylmagnesium is several times faster than by organomagnesium-halide reagents¹³, but metallation by the second alkyl group is somewhat slower⁷. The nature of R, however, can be significant. In metallations of 1-hexyne by organomagnesium-halide reagents in Et_2O , e.g., the order allyl > isopropyl > ethyl > propyl > methyl spans¹² a rate range of ≈ 70 , and metallation by a series of arylmagnesium halides shows⁹ a ρ of -2.5 ;
3. Electron-withdrawing groups in the alkyne increase metallation rate¹⁴. As a consequence, the metallation of ethoxyacetylene is achieved in a few minutes at 0°C ¹⁵:



4. Reactions are more rapid in tetrahydrofuran (THF) than in Et_2O ^{10,16,17}, and addition of R_3N to Et_2O increases rates^{14,18,19}. Use of hexamethylphosphoramide (HMPA) as the solvent accelerates metallation rate; e.g., 1-heptyne is metallated by isopropylmagnesium chloride in cooled HMPA^{20,21}.

Reactions of acetylene, the simplest alkyne, with organomagnesiums can result either in mono or dimetallation. Dimetallation is achieved, e.g., by passing acetylene through ethylmagnesium bromide in Et_2O :

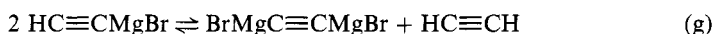


Rates depend on reaction parameters, but 12–24 h are common for preparations of a few tenths of a mole of di(bromomagnesio)acetylene and 30–35 h are needed for a 1-mol reaction²². The product separates from the solution as a viscous oil that contains ca. 2 mol of Et_2O per mol of Mg ²³. The Et_2O can be decanted and the oil dissolved in CH_2Cl_2 ²⁴ or CHCl_3 ²⁵. If most of the Et_2O is replaced by benzene before addition of acetylene, the product separates as a gray powdery suspension²⁶. In another preparation, acetylene is passed into ethylmagnesium bromide in THF at a rate that maintains a T of $50\text{--}55^\circ\text{C}$ ²⁷.

The preparation of ethynylmagnesium bromide free from di(bromomagnesio)-acetylene, presents a challenge:



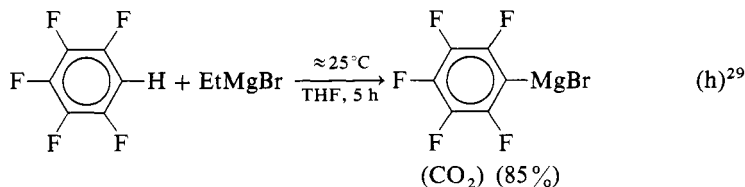
The disproportionation equilibrium combined with the relative insolubility in some solvents of di(bromomagnesio)acetylene make it difficult to form ethynylmagnesium bromide uncontaminated by the di(bromomagnesio) compound:



The preparation can be achieved, however, by an inverse addition procedure: ethylmagnesium bromide is added slowly to a THF solution kept at ca. 30°C through which acetylene is passed rapidly.²⁸

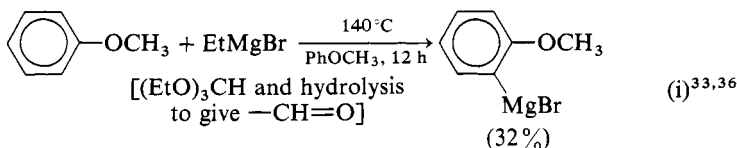
(ii) Arylmagnesiums and Vinylmagnesiums. Hydrogens attached to the sp²-hybridized carbon of aryl and vinyl compounds are less acidic than those on triply bonded carbons, and this is reflected in a more difficult metal-hydrogen exchange.

Formation of arylmagnesiums by metallation is observed only when the aryl compounds have particularly favorable substitution. The metallation of pentafluorobenzene occurs readily at RT:

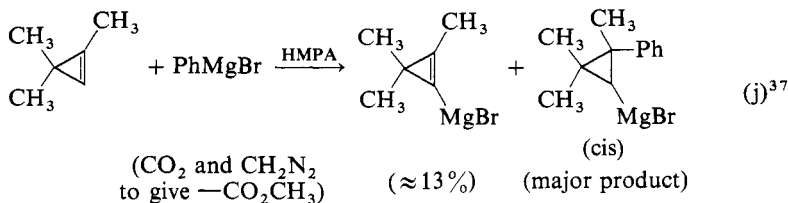


This and other metallations of polyfluoro^{30,31} and polychloro³² aromatics are aided by the strongly electron-withdrawing halogens.

Orthometallation is observed in aryl ethers^{33–35} and also in an aryl tertiary amine³⁴ when vigorous conditions are used:

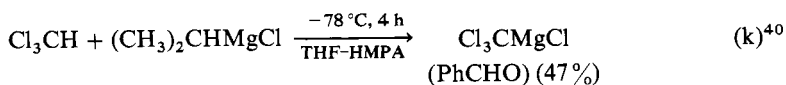


Metallation of cyclopropenes occur readily. Even in favorable cases, however, yields are low, because addition is even more rapid (see §5.4.2.5.1), e.g.:



The =CH acidity is enhanced, of course, by the increased s character of carbons of highly strained rings.³⁸

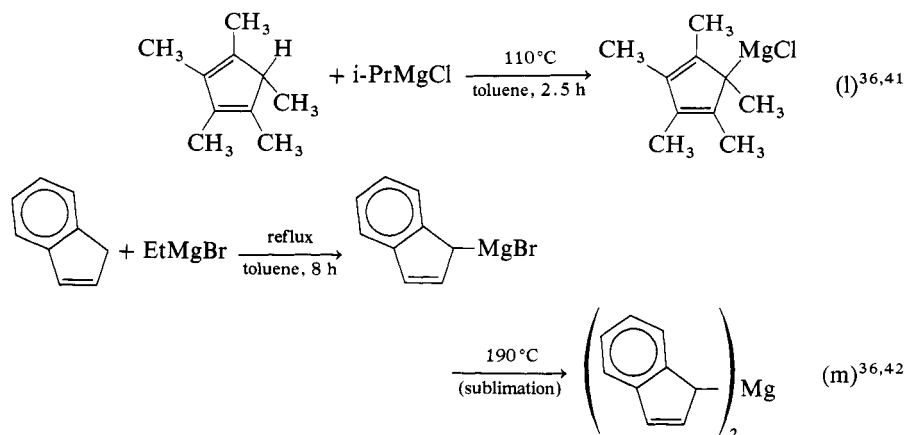
(iii) α-Haloorganomagnesiums. Magnesium-hydrogen exchange at saturated, non-conjugated carbons is noted only for polyhalomethanes³⁹:



The resulting organomagnesiums decompose (by MgX₂ elimination) and must be prepared and used at low T. The exchange is facilitated and the stability of the α-haloorganomagnesiums is enhanced by HMPA.

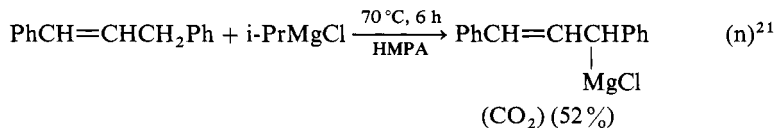
(iv) Conjugated Organomagnesiums. Metallations of saturated carbons of some hydrocarbons are feasible if particularly stable anions result. Cyclopentadiene and

substituted cyclopentadienes, including indene and fluorene, can be converted quantitatively to organomagnesiums:



These are systems that form aromatic carbanions ($4n + 2\pi$ electrons). Such reactions are readier if HMPA is present²⁰. Indene in THF, e.g., is metallated rapidly at RT by diethylmagnesium if sufficient HMPA is added; two HMPA's per dialkylmagnesium are required to maximize the effect⁴³.

Use of HMPA also permits metallation of somewhat weaker acids; e.g., with isopropylmagnesium chloride in HMPA, triphenylmethane reacts at 90°C, diphenylmethane at 100°C, and 1,3-diphenylpropene at 70°C²¹:



Metallation of these hydrocarbon is unsuccessful in other solvents.

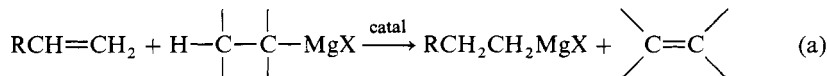
(H. G. RICHEY, JR.)

1. Early work (to ca. 1950) is reviewed comprehensively in M. S. Kharasch, O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 66. A briefer review of developments into the early 1960s is provided in S. T. Ioffe, A. N. Nesmeyanov, *The Organic Compounds of Magnesium, Beryllium, Calcium, Strontium and Barium*, North-Holland Publ., Amsterdam, 1967, p. 45. An excellent newer review that includes references through 1971 is 1K. Nützel, in *Methoden der Organischen Chemie Houben-Weyl*, 4th ed., Vol. 13/2a, George Thieme Verlag, Stuttgart, 1973, p. 134. An authoritative and more recent but brief review is W. E. Lindsell, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, ed., Pergamon Press, Oxford, 1982, Chapter 4.
2. In addition to the reviews listed in ref. 1, formation of organomagnesiums by metallation of terminal acetylenes is reviewed in ref. 3, p. 373, and T. F. Rutledge, *Acetylenic Compounds*, Reinhold Books, New York, 1968, p. 71.
3. V. Jäger, H. G. Viehe, in *Methoden der Organischen Chemie Houben-Weyl*, 4th ed., Vol. 5/2a, Georg Thieme Verlag, Stuttgart, 1977, p. 373.
4. J. Cymerman, I. M. Heilbron, E. R. H. Jones, *J. Chem. Soc.*, 144 (1944).
5. For example, J. W. Kroeger, J. A. Nieuwland, *J. Am. Chem. Soc.*, 58, 1861 (1936).

6. In addition to the examples of 1-alkynylmagnesiums prepared this way that are given in refs. 1 and 2, more examples and their preparative use can be found in ref. 3, p. 408.
7. S. K. Podder, E. W. Smalley, C. A. Hollingsworth, *J. Org. Chem.*, **28**, 1435 (1963).
8. R. E. Dessy, J. H. Wotiz, C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 358 (1957).
9. R. E. Dessy, R. M. Salinger, *J. Org. Chem.*, **26**, 3519 (1961).
10. Y. Pocker, J. H. Exner, *J. Am. Chem. Soc.*, **90**, 6764 (1968).
11. Although exceptions are claimed: H. Hashimoto, T. Nakano, H. Okada, *J. Org. Chem.*, **30**, 1234 (1965).
12. J. H. Wotiz, C. A. Hollingsworth, R. Dessy, *J. Am. Chem. Soc.*, **77**, 103 (1955).
13. J. H. Wotiz, C. A. Hollingsworth, R. E. Dessy, *J. Am. Chem. Soc.*, **78**, 1221 (1956).
14. J. H. Wotiz, C. A. Hollingsworth, R. E. Dessy, *J. Org. Chem.*, **20**, 1545 (1955).
15. J. F. Arens, D. A. Van Dorp, *Recl. Trav. Chim. Pays-Bas*, **67**, 973 (1948).
16. L. Brandsma, H. D. Verkruisje, *Synthesis of Acetylenes, Allenes and Cumulenes*, Elsevier Scientific, Amsterdam, 1981, p. 18.
17. Although not in every instance: J. H. Wotiz, G. L. Proffitt, *J. Org. Chem.*, **30**, 1240 (1965).
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34. F. Challenger, S. A. Miller, *J. Chem. Soc.*, 894 (1938).
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38. D. J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York, 1965, p. 48.
39. For a brief review, see J. Villiéras, *Organomet. Chem. Rev., Sect. A*, **7**, 81 (1971).
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41. P. J. Fagan, J. M. Manriquez, E. A. Maatta, A. M. Seyam, T. J. Marks, *J. Am. Chem. Soc.*, **103**, 6650 (1981).
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5.4.2.5.3. by Transfer of the Elements of Magnesium Hydride to Alkenes, Especially with Catalysis by Ti Compounds.

In the presence of a suitable catalyst, terminal alkenes are converted into organomagnesium-halides by formal transfer of H and MgX from an organomagnesium-halide reagent to the alkene¹:



The reagent must have a β -H and the alkene usually is only monosubstituted ($\text{RCH}=\text{CH}_2$).

5.4. Formation of Bonds between Elements

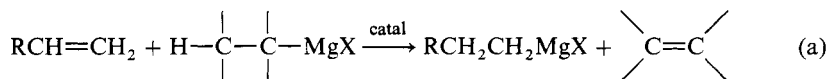
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16. L. Brandsma, H. D. Verkruisje, *Synthesis of Acetylenes, Allenes and Cumulenes*, Elsevier Scientific, Amsterdam, 1981, p. 18.
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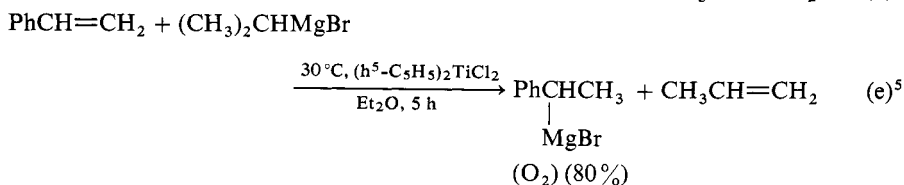
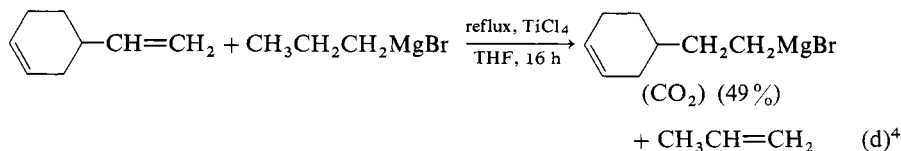
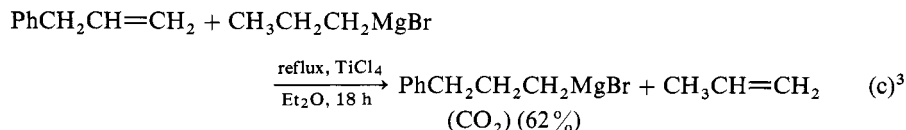
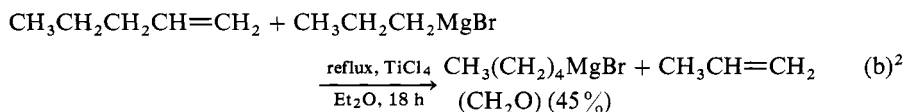
5.4.2.5.3. by Transfer of the Elements of Magnesium Hydride to Alkenes, Especially with Catalysis by Ti Compounds.

In the presence of a suitable catalyst, terminal alkenes are converted into organomagnesium-halides by formal transfer of H and MgX from an organomagnesium-halide reagent to the alkene¹:



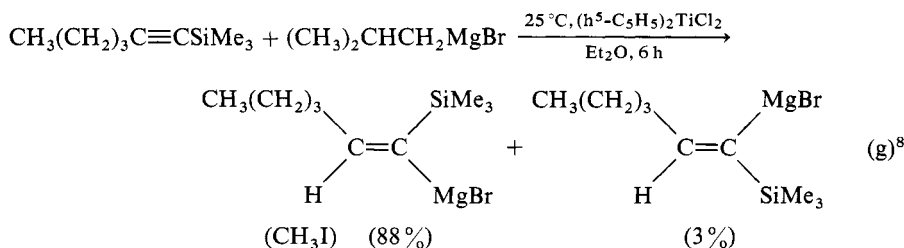
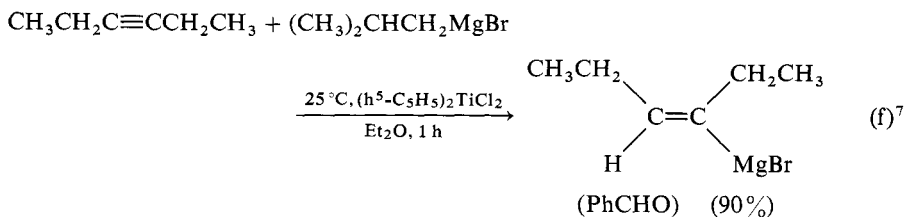
The reagent must have a β -H and the alkene usually is only monosubstituted ($\text{RCH}=\text{CH}_2$).

The catalyst is usually a Ti(IV) compound; typically 1–3 % of the molar amount of the organomagnesium is used:



Propene is also a product in these reactions, which are reversible; however, loss of this volatile alkene must favor formation of the new organomagnesium-halide reagents. The terminal (primary) reagent predominates. Addition to styrene provides an exception; the secondary (but in this instance also the more stable) organomagnesium-halide is the major product. Note that addition is observed only to the monosubstituted double bond in Eq. (d). In fact, in the absence of other functional groups such additions are ordinarily observed only to monosubstituted alkenes. Isomerization of the 1-alkene to a 2-alkene is a competing reaction; e.g., *cis*- and *trans*-2-pentene are formed in reactions of 1-pentene².

Additions to alkynes⁷ and alkynylsilanes^{7–9} are mainly syn:



In additions to alkynylsilanes, the Mg is attached exclusively to the carbon bonded to Si. Additions also are observed to dienes⁵, alkenols^{10,11}, alkynols¹², and to dienes⁹ and alkynols^{13–15} having a trimethylsilyl substituent attached to one of the multiply bonded carbons.

With 1-octene, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ is a more reactive catalyst¹⁶ for the alkylmagnesium-alkene exchange than is TiCl_4 . Yields of 1-octylmagnesium increase at first but then decrease slowly owing to reversibility of the exchange and the competing isomerization of 1-octene to 2-octene. Yields and rate do not differ when the organomagnesium is Pr_2Mg , $n\text{-Bu}_2\text{Mg}$, $i\text{-Bu}_2\text{Mg}$, $s\text{-Bu}_2\text{Mg}$, $i\text{-BuMgCl}$, $i\text{-BuMgBr}$, or $i\text{-BuMgI}$. Reaction is slower, however, when Et_2Mg is used. With $t\text{-Bu}_2\text{Mg}$, exchange is slow but isomerization of 1-octene to 2-octene fast, so yields of 1-octylmagnesium are low.

This exchange procedure for preparing organomagnesium halides often offers no advantages over their preparation from alkyl halides. It is useful, however, when an alkene is more available than the appropriate alkyl halide. It may also be useful when side reactions (e.g., coupling, dehydrohalogenation, etc.) severely limit the yields of organomagnesium halides in preparations from halides, e.g., the preparation of 1-phenylethylmagnesium halide in Eq. (e).

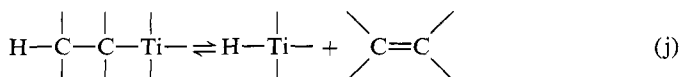
The mechanism of these reactions involves formation of a Ti hydride followed by a chain of reactions: (1) addition of the Ti hydride to the alkene to form the less substituted organotitanium:



(2) Ti-Mg exchange:

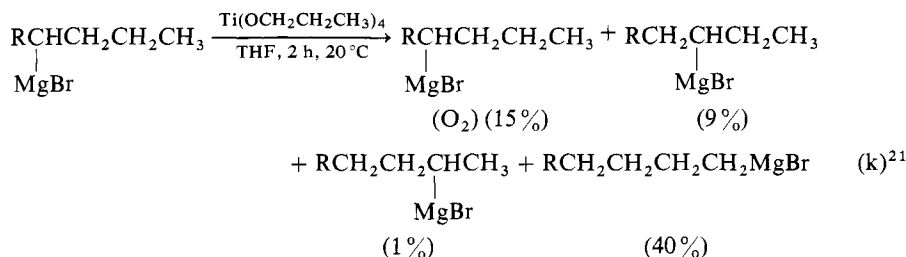


and (3) elimination to regenerate the Ti hydride:



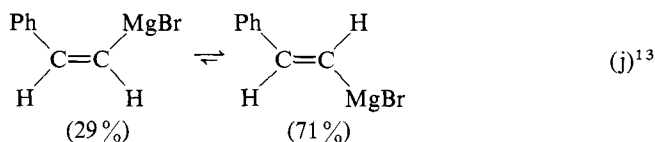
This process is related, of course, to the Ti-catalyzed Mg hydride additions discussed in §5.4.2.4.1. It is evident why a MeMg does not lead to isomerization¹⁶. Both Ti(III) and Ti(IV) hydrides can be the active species. With $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$, a Ti(III) species, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiH}$, is likely¹⁷. The 1-alkene to 2-alkene isomerization is attributed to catalysis by $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiR}$, in which R comes from the alkene or the organomagnesium¹⁶. Organomagnesium halide-alkene exchanges are also observed in the presence of catalytic amounts of ZrCl_4 ³, VCl_4 ³, NiCl_2 ^{18,19} and FeCl_3 ²⁰, although catalytic efficiency is generally lower.

Transition-metal compounds also catalyze the rearrangement of organomagnesium halides^{2,18,19,21}, e.g.:



where $R = CH_3CH_2CH_2CH_2-$. Such reactions proceed by steps similar to those of the exchanges: conversion by Mg—Ti exchange of the organomagnesium halide to small amounts of an organotitanium, which, before reconversion to an organomagnesium-halide reagent, can isomerize by elimination to a Ti—H species and an alkene followed by their recombination. Because these isomerizations are reversible, they are useful principally for converting organomagnesium halides to more stable isomers, e.g., in Eq. (i), a secondary to a primary reagent. Because of rapid loss of catalytic activity as well as side reactions of the organometallics (which increase with increasing amounts of catalyst), equilibrium concentrations of organomagnesium halides are not achieved, and material balances are mediocre. In the example above, the catalyst (3% of the mol amount of organomagnesium-halide reagent) is added in portions. If it is added all at once, the extent of isomerization is less. Note that in the reaction above, some addition to disubstituted alkenes (3-octene and 2-octene) must occur.

Nickel salts catalyze the cis-trans isomerization of vinylmagnesium halides²²⁻²⁴. In the presence of a small amount of $(Ph_3P)_2NiCl_2$, $NiCl_2$ or $Ni(PPh_3)_4$, either the cis- or the trans-organomagnesium-halide reagent in Eq. (i) is converted in 5 h at Rt to an equilibrium mixture:



(H. G. RICHEY, JR.)

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5.4.3. Formation of the Carbon—Group IIA-Element Bond (Except Mg)

5.4.3.1. from the Elements

This topic is dealt with in §5.10.2.

5.4.3.2. from the Group-IIA Metals and Their Alloys

Organo -Ca, -Sr and -Ba derivatives are prepared from the metals. With Be, however, the compounds are produced from anhydr BeCl_2 and organomagnesium-halide reagents or lithium alkyls. In principle, RBe derivatives can also be formed from Be metal. Thus, a Be mirror disappears by the effect of alkyl radicals¹, but such reactions cannot be used in practice. Beryllium dialkyls also can be prepared from olefins and H_2 with the metal in the presence of small amounts of Br_2 or I_2 , and by the electrolysis of $\text{M}[\text{AlR}_3\text{R}']$ complexes ($\text{M} = \text{Na}, \text{K}$; $\text{R} = \text{alkyl}$; $\text{R}' = \text{alkyl, alkoxy}$) using anodes of pure Be. However, laboratory application is limited owing to the lack of detailed information and the need for expensive apparatus.

In all reactions O_2 and moisture must be excluded. Therefore, all operations must be performed in vacuum or under Ar. Nitrogen cannot be used for reactions with Sr and Ba metal because of the risk of nitride formation.

Most R_2M compounds are pyrophoric. Therefore, they must be handled with extreme caution.

(K. JACOB, K.-H. THIELE)

1. F. Paneth, H. Loleit, *J. Chem. Soc.*, 369 (1935).

5.4.3.2.1. by Organic Halides with the Metal.

There is little information on reactions of Be with alkyl and aryl halides:



where $\text{X} = \text{Cl, Br, I}$. The rate and the yield depend on the purity of the metal, the solvent, halogen and T. The metal need not be pure, but its surface must not be coated by an oxide layer. Activation is possible by adding HgCl_2 or Hg metal + I_2 .

Low-boiling alkyl halides do not react with Be in an acceptable time; however, they do if the alkyl, cycloalkyl, aralkyl and aryl halides have $\text{bp} = 120^\circ\text{--}200^\circ\text{C}$. Hydrocarbons are formed as byproducts whose quantity increases with T. These coupling products are formed mainly at $>200^\circ\text{C}$.

The formation of organoberyllium halides is favored by solvents, especially aromatic hydrocarbons and ethers. The best results (yield ca. 70%) are obtained in boiling Et_2O after activation of Be with Hg or from anhydr BeCl_2 in ether. However, the alkylberyllium halides obtained are ether complexes from which the ether cannot be removed in vacuum on heating. The rate is slow when alkyl chlorides are used, hence, the bromides and iodides are preferred.

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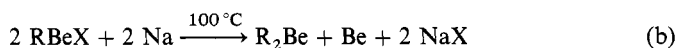


where $\text{X} = \text{Cl}, \text{Br}, \text{I}$. The rate and the yield depend on the purity of the metal, the solvent, halogen and T. The metal need not be pure, but its surface must not be coated by an oxide layer. Activation is possible by adding HgCl_2 or Hg metal + I_2 .

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These organoberyllium halides can be dehalogenated by heating with Na, K, Mg, Al or Zn metal:



Calcium metal reacts with organic halides in suitable solvents to form organocalcium halides:



(X = Cl, Br, I).

The quality of the Ca metal determines the course of reaction. The rate is slow at a high purity but increases in the presence of Mg metal, whereas Na metal promotes coupling to form CaCl_2 and hydrocarbons. Activation of Ca is possible with Hg metal or HgCl_2 , which, however, involves the risk of product contamination by RHgX derivatives.

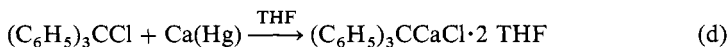
The RCaX derivatives (R = n-alkyl, i-alkyl) may be obtained in benzene, toluene and cyclohexane at $40^\circ\text{--}80^\circ\text{C}$ in yields of 40–75%³. Coupling cannot be avoided completely; therefore, the products insoluble in hydrocarbons become contaminated by CaCl_2 . Another disadvantage is the difficulty of removing the unreacted finely divided metal.

The preparation of RCaX derivatives in hydrocarbons takes 1–2 days. Acceptable amounts of aryl derivatives cannot be synthesized in this way.

Alkyl chlorides and bromides react slowly with Ca metal, but the rate can be accelerated by the addition of the corresponding iodides.

Alkyl and aryl iodides react quickly with activated Ca metal in ethers to give organocalcium iodides⁴. The metal can be activated with a previously prepared RCaI solution. Coupling is unavoidable, but these side reactions decrease with T. Particularly high yields can be obtained in tetrahydrofuran (THF) at -40° to -70°C , e.g.⁵, CH_3CaI , 60%; $\text{C}_2\text{H}_5\text{CaI}$, 65%; $n\text{-C}_3\text{H}_7\text{CaI}$, 73%; $n\text{-C}_7\text{H}_{15}\text{CaI}$, 40%; $\text{C}_6\text{H}_5\text{CaI}$, 97%; $1\text{-C}_{10}\text{H}_7\text{CaI}$, 94%.

Organic chlorides and bromides react slowly with Ca metal, but the reactions can be initiated by addition of ca. 10 mol% of the corresponding iodides. Nevertheless, the yields remain lower than when iodides are used. Exceptions are the reactions of chlorides with more strongly polar C—Cl bonds. Thus, $(\text{C}_6\text{H}_5)_3\text{CCaCl} \cdot 2 \text{THF}$ is obtained in nearly quantitative yield⁶:



The THF can be removed in vacuum at ca. 80°C .

Benzyl halides also react with Ca metal, but mainly hydrocarbons with only small amounts of $\text{C}_6\text{H}_5\text{CH}_2\text{CaX}$ derivatives are formed.

Organocalcium halides cleave ethers. Ether solutions are therefore not stable and must be used quickly. The solutions in Et_2O can be stored at -20°C for days. The half-life of CH_3CaI in THF is 13 days at RT. With most RCaX compounds, however, reaction with THF proceeds quickly and occurs even at -78°C .

Definite $\text{IRCa} \cdot \text{O}_2\text{C}_4\text{H}_8$ complexes (R = C_6H_5 , $2\text{-CH}_3\text{C}_6\text{H}_4$, $3\text{-CH}_3\text{C}_6\text{H}_4$) can be separated from ether by addition of 1,4-dioxane. The dioxane is removed in vacuum at

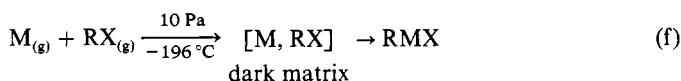
110°–120°C leaving⁷ pure RCaI. Corresponding 1:1 complexes are formed with dimethoxyethane (DME), diglyme, tetramethylethylenediamine (TMED) and diaza-(1,4)-bicyclo(2.2.2)octane.

Reactions of organic halides with Sr and Ba metal are difficult to realize and are carried out successfully only with iodides. Arylstrontium iodides, RSrI (R = C₆H₅, 2-CH₃C₆H₄, 3-CH₃C₆H₄, 1-C₁₀H₇, 2-thienyl) are formed as etherates from activated Sr metal and the appropriate aryl iodides in Et₂O. Benzene may also be used after addition of THF sufficient for the formation of 1:1 complexes⁸; THF is a more suitable solvent but requires Sr and Ba amalgam and a low T to prevent ether cleavage and the isolation of crystalline products:



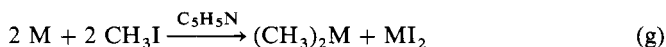
where if M = Sr, R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉ and n = 2, 3; if M = Ba, R = C₂H₅ and n = 1. The yields obtained are 60–85%⁹.

Cocondensation of gaseous metal with organic halides forms organocalcium halides and the corresponding Sr and Ba compounds⁹:



This method is not limited to the iodides. It also allows the preparation of alkylmetal chlorides and bromides but requires the necessary equipment. In principle n-, i- and t-alkyl derivatives can be prepared in this way. However, these reactions are unsuitable for larger scale preparations.

By contrast, dimethyl Ca, Sr and Ba compounds are formed by interaction of CH₃I with freshly prepared foils of the metals in pyridine¹⁰:



where M = Ca, Sr, Ba. The metal iodides can be removed from the insoluble (CH₃)₂M compounds by extraction with boiling pyridine. The remaining pyridine attached to the diorganyls is removed in vacuum.

(K. JACOB, K.-H. THIELE)

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5.4. Formation of Bonds between Elements

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5.4.3. Formation of the Carbon—Group IIA—Element Bond

5.4.3.2. from the Group-IIA Metals and Their Alloys

5.4.3.2.2. by Organomercury, Organocadmium or Organozinc Compounds with the Metal.

The carbon—Hg bond cleavage to form carbon—Be bonds results from diorgano-mercurials with Be amalgam:



where R = CH₃, C₂H₅, C₆H₅, 4-CH₃C₆H₄. The reactions occur at 110°–170°C, in ca. 2–4 days¹. Beryllium dialkyls can be prepared in yields of 50–60%, but with diaryl compounds, yields are low.

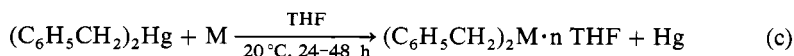
Aromatic hydrocarbons as solvents favor² the formation of (C₆H₅)₂Be. The activation of Be metal by Hg or by previous treatment with HgCl₂ or (C₂H₅)₂Be in ether is necessary for initiation.

The R₂Be derivatives obtained are not donor complexes. Disadvantages are, e.g., the long reaction times and the necessity of carrying out the experiments under pressure in sealed tubes.

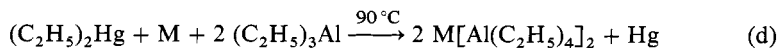
Formation of carbon—Ca bonds occurs when Ca metal interacts with Hg diaryls in tetrahydrofuran (THF). Good yields of Ca diaryls are obtained as THF complexes:



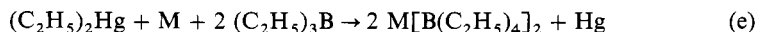
where R = C₆H₅, 2-, 3-, 4-CH₃C₆H₄, 1-C₁₀H₇, 2-thienyl. Diethylether and aromatic hydrocarbons are less suitable solvents. Calcium dialkyls are not prepared in this way, but the dibenzyl compounds of Ca, Sr and Ba are⁴:



where M = Ca, Sr, Ba. The reactions take another course in the presence of R₃Al or R₃B, leading to anionic [R₄Al][−] or [R₄B][−], respectively, with carbon—M bonds in the form of weak M⋯R⋯M' bridges (M' = B, Al)⁵:

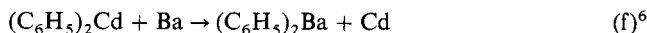


where M = Ca, Sr;

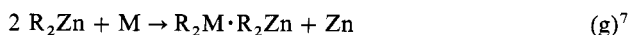


where M = Ca, Sr, Ba.

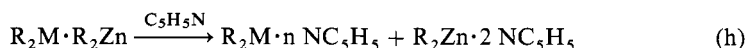
These carbon—M bonds are also formed in reactions of Ca, Sr and Ba with Cd and Zn dialkyls. In this way, diphenylbarium is obtained:



Zinc dialkyls react with alkaline-earth metals, forming dialkyl compounds that combine with further R₂Zn to give complexes:



where $M = \text{Ca, Sr, Ba}$; $R = \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9$. These complexes can be split by donors such as pyridine and are converted into complexes of the constituents⁸:



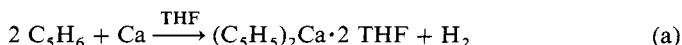
Mercury dialkyls are strong respiratory poisons and toxic to the skin. Therefore, all operations must be carried out in closed apparatus. **The handling of sealed tubes under pressure is dangerous and should be carried out in a special room only by experienced persons.**

(K. JACOB, K.-H. THIELE)

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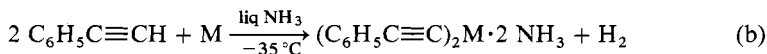
5.4.3.2.3. by Acidic Hydrocarbons with the Metal to Evolve H_2 .

Acidic hydrocarbons react with Ca, Sr and Ba metal in polar solvents with cleavage of carbon—hydrogen and formation of carbon—M bonds; e.g., Ca reacts with C_5H_6 in tetrahydrofuran (THF) in which H_2 evolves and $(\text{C}_5\text{H}_5)_2\text{Ca}$ is formed as a THF complex¹:



Dimethylformamide is required for the corresponding reaction of Sr metal. Barium metal does not react with C_5H_6 under similar conditions.

Solutions of Ca, Sr and Ba metal in liq NH_3 react with acidic hydrocarbons. Thus the complexes $(\text{C}_5\text{H}_5)_2\text{Ca} \cdot n \text{NH}_3$ and $(\text{C}_9\text{H}_7)_2\text{Ca} \cdot n \text{NH}_3$ are formed from cyclopentadiene or indene with Ca metal². Analogously the acidic hydrogen atoms of alkynes are substituted by alkaline-earth metals³:



where $M = \text{Ca, Sr, Ba}$.

The carbon—M bonds also form by cocondensation of acidic hydrocarbons with alkaline-earth metal vapor⁴. In this way the cyclopentadienides and indenyl compounds of Ca, Sr and Ba that are difficult to obtain by other methods for Sr and not at all for Ba can be prepared nearly quantitatively. Because of the required vacuum techniques, this method is suitable for the preparation of small amounts only.

(K.-H. THIELE, K. JACOB)

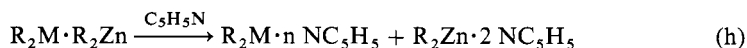
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5.4. Formation of Bonds between Elements

5.4.3. Formation of the Carbon—Group IIA—Element Bond

5.4.3.2. from the Group-IIA Metals and Their Alloys

where $M = \text{Ca, Sr, Ba}$; $R = \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9$. These complexes can be split by donors such as pyridine and are converted into complexes of the constituents⁸:



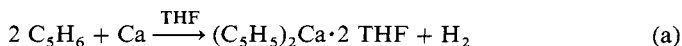
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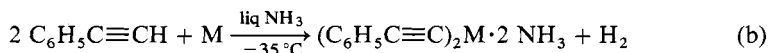
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5.4. Formation of Bonds between Elements

303

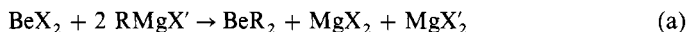
5.4.3. Formation of the Carbon—Group IIA-Element Bond

5.4.3.3. from Group-IIA Halides and Related Compounds

5.4.3.3. from Group-IIA Halides and Related Compounds**5.4.3.3.1 with More Active Organometallics.**

Diorganylberylliums¹, BeR₂, are formed in high yields by metathetical exchange between organometallics of more electropositive metals and Be halides or related Be compounds^{2,3}. Organomagnesium-halide reagents or organolithiums are employed in these alkylations, but in certain cases organosodium or -potassium reagents are useful. Organometallics of Ca, Sr and Ba are, at best, produced only in equilibrium processes from the respective halides so that such reactions are of little preparative value⁴. No examples of Ra organometallics are known.

(i) From Organomagnesium-Halide Reagents. The formation of BeR₂ compounds by:



is a standard procedure for dialkyl and a few diaryl compounds (R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu, n-pentyl, neo-pentyl, benzyl, Ph, p-tolyl, mesityl)^{2,3}. The chiral BeR₂ compound {R = [(1S, 2S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]methyl (85 %)}⁵, useful for asymmetric reduction of prochiral ketones, is prepared similarly. Conditions of typical reactions are outlined in Table 1. Anhydrous BeX₂ (X = Cl or Br) is required and is best prepared by direct reaction of the metal with X₂ vapor in a hot tube (500°C), followed by resublimation. Diethyl ether is the most common solvent. A slight xs organomagnesium-halide solution is added to a solution of BeX₂, or vice versa, under an inert atmosphere and the mixture maintained at ambient or reflux T until reaction is complete. The ether solution of BeR₂ is usually separated from MgX₂ before workup. Because MgCl₂ is less soluble in Et₂O than the other Mg halides, it is often preferable to use RMgCl and BeCl₂ for these preparations. Gel formation during mixing BeCl₂ and RMgX can be a practical problem, especially in large-scale reactions. It may be overcome by using less concentrated solutions or by addition of granular Cl₂Mg·OEt₂ to the mixture^{2,10}.

TABLE 1. PREPARATION OF BeR₂ BY ORGANOMAGNESIUM-HALIDE REAGENTS WITH BeCl₂

RMgX	Solvent	Product (yield, %)	Refs.
MeMgI	Et ₂ O	BeMe ₂ (85–90) ^a	2,3,6
CD ₃ MgI	Me ₂ S	Be(CD ₃) ₂ ^b	7
EtMgBr	Et ₂ O	BeEt ₂ (80–90) ^c	2,3
n-BuMgBr	Et ₂ O	BeBu ₂ -n ^b	8
n-BuMgI	Benzene	BeBu ₂ -n (41) ^c	9
i-BuMgCl	Et ₂ O	BeBu ₂ -i ^b	8
t-BuMgCl	Et ₂ O	BeBu ₂ -t(OEt ₂) (55–65) ^d	10
PhMgCl	Et ₂ O	BePh ₂ (OEt ₂) _{1 2} ^{b,c}	12

^a A larger scale reaction yields 4.4 mol (64 %), ref. 5.

^b Yield not quoted.

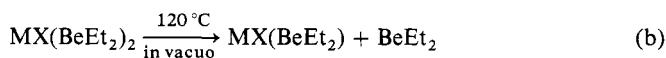
^c Prepared in benzene; R = Et (35 %), R = i-Bu (70 %), R = Ph (77 %); ref. 9.

^d Converted to ether-free BeBu₂-t (40 %) using BeCl₂; ref. 11.

The product, BeR_2 , is initially obtained as an etherate or ether solution by distillation in vacuo. For the more stable BeMe_2 , codistillation with Et_2O may be carried out at 220°C ⁶. For higher alkyls containing β -hydrogen atoms, thermal decomposition to 1-alkene and beryllium hydride must be avoided by keeping T as low as possible (e.g., $< 70^\circ\text{C}$ when $\text{R} = \text{i-Bu}$, t-Bu , t-Bu)⁸. In the preparation of $\text{Ph}_2\text{Be} \cdot 2 \text{OEt}_2$ using a slight deficiency of PhMgBr , all the halide may be removed by precipitation with dioxane and the product crystallized from the halide-free solution¹².

Solvent evaporation in vacuo reduces the ether content of BeR_2 products but removal of all solvate may present difficulties^{2,3}. Repeated sublimation of BeMe_2 removes final traces of Et_2O ; alternatively a concentrated solution of BeMe_2 in ether may be added to xs toluene and, on boiling, ether-free BeMe_2 crystallizes.

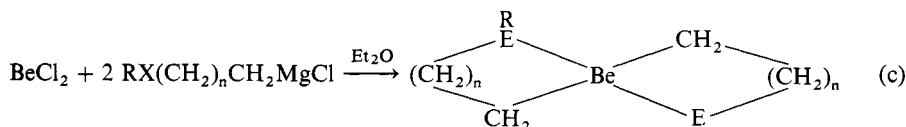
The liquid, ether-free alkyls, BeR_2 ($\text{R} = \text{Et}$, n-Pr , i-Pr , n-Bu , i-Bu) can be obtained by prolonged refluxing under reduced pressure [10^{-2} to 10^3 torr (1.3 – 0.13 Nm^{-2})] at 50° – 60°C ⁸. However, ether cannot be removed by such a process from $\text{R}_2\text{Be} \cdot \text{OEt}_2$ ($\text{R} = \text{t-Bu}$, neo-pentyl, Bz). Heating $(\text{t-BuCH}_2)_2\text{Be} \cdot \text{OEt}_2$ at 195° – 230°C forms⁹ BeMe_2 . Coordinated ether of $\text{t-Bu}_2\text{Be} \cdot \text{OEt}_2$ may be transferred to added BeCl_2 and the free $\text{Be}(\text{Bu-t})_2$ isolated by vacuum distillation¹¹. Ether-free BeEt_2 may be obtained via complexation with salts to form¹² $\text{MF}(\text{BeEt}_2)_2$ ($\text{M} = \text{K}$, Rb , NMe_4) and $\text{KCN}(\text{BeEt}_2)_4$. These complexes liberate free BeEt_2 on heating to 120°C :



Alternatively, stirring $\text{KF}(\text{BeEt}_2)_2$ in benzene at 80°C gives insoluble $\text{KF}(\text{BeEt}_2)$ and soluble BeEt_2 .

Dimethylberyllium may be synthesized in Me_2S ; solvation occurs, but free BeMe_2 can be obtained by repeated sublimation⁷. Using organomagnesium halides formed in benzene (alkyl:halogen ratio > 1) solutions of uncoordinated BeR_2 ($\text{R} = \text{Et}$, n-Bu , $\text{n-C}_5\text{H}_{11}$, Ph , p-tolyl) are obtained, and from these solutions free dialkyl compounds should be isolable, although, as yet, this is realized⁸ only for $\text{Be}(\text{Bu-n})_2$ ⁹.

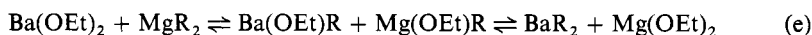
Ether-free spirocyclic complexes are formed from organomagnesium halide reagents incorporating oxygen or sulfur groups [if $\text{R} = \text{Et}$, $\text{E} = \text{S}$, $n = 2$ (62%); if $\text{R} = \text{Me}$, $\text{E} = \text{O}$, $n = 3$ (45%)]^{2,3}:



Alkylberyllium chlorides form from equimol RMgCl and BeCl_2 in ether, e.g., where $\text{R} = [(1\text{S}, 2\text{S})\text{-6,6-dimethylbicyclo}[3.1.1]\text{heptan-2-yl}]$ methyl (75%)⁵ or (R) -2-methylbutyl (90% as monoetherate)¹⁴:



Reactions between $\text{Ba}(\text{OR})_2$, especially $\text{R} = \text{Et}$, and organomagnesiums lead to equilibrium mixtures of species¹³:



The organoberyllium products are insoluble in aromatic solvents and THF. Evidence for the formation of Ba—C bonds is adduced from the ability of such mixtures to promote polymerization reactions and to combine with 1,1-diphenylethene.

(ii) From Organolithiums. Because organolithiums are preparable in hydrocarbons their use in formation of BeR₂:



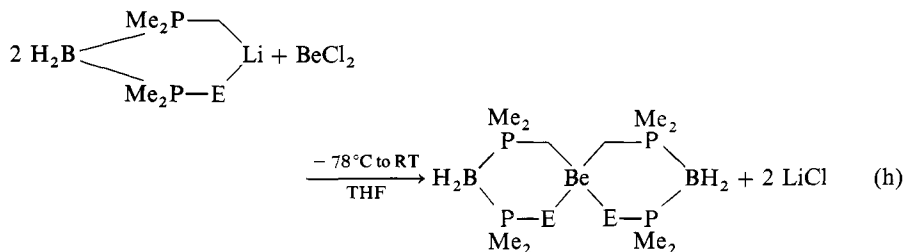
should result in ether-free products. In fact the few detailed procedures for simple alkyl derivatives employ some ether in the solvent. Syntheses in mixed hydrocarbon-ether solvents are available for BeR₂ (R = Me¹⁶, n-Bu¹⁷, i-Bu¹⁷, s-Bu¹⁸, t-Bu¹⁹) and are similar to related organomagnesium-halide reactions. The optically active derivative (+)-bis[(R)-2-methylbutyl]beryllium (40%) is also formed in petroleum ether, containing some Et₂O from BeCl₂, and the Li reagent²⁰.

Diarylberyllium compounds are made from aryllithiums, and this method is recommended for the preparation²¹ of pure BePh₂ in Et₂O, although complete removal of solvated Et₂O is not possible. Similarly, (C₆F₅)₂Be·n OEt₂ (n ≈ 0.7) is obtained from LiC₆F₅ in ether, but attempts at purification by **distillation result in mild explosions** at 130°C²². The mixed compound, h⁵-C₅H₅BePh, is formed by²³:

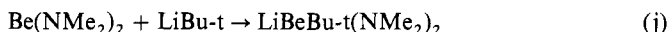
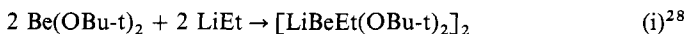


Alkynyl compounds (RC≡C)₂Be·n OEt₂ (R = Me, t-Bu, Ph), are products from BeCl₂ and the corresponding alkynyllithium in ether²⁴. The solvated ether cannot be removed under reduced pressure from (PhC≡C)Be·OEt₂, but it may be displaced by other ligands, including THF, NR₃ and pyridine (py). The structurally characterized adduct [(MeC≡C)₂Be·NMe₃]₂, which crystallizes from benzene-hexane²⁵, and similar adducts may be formed from (RC≡C)₂Be·n OEt₂ (R = Me, t-Bu), but desolvation of the latter compound also occurs in vacuo [10⁻³ torr (0.13 Nm⁻²), 25°C] to give insoluble, virtually ether free-compounds that are probably polymeric. Polymeric decomposition products arise² from reaction of vinylolithium and BeCl₂.

Novel, sublimable spirocyclic beryllium complexes are synthesized by:

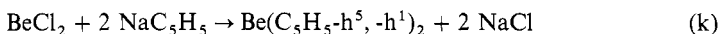


[E = O (11%)²⁶, CH₂ (36%)²⁷]. Complex bimetallic derivatives result from combination of alkylolithium and beryllium compounds, e.g.²⁴:

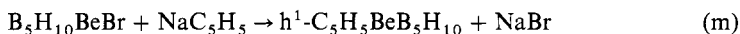
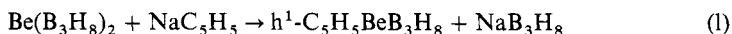


Anthracene radical anions formed by reaction with Li metal react with BeCl₂ in THF giving a complex, σ-bonded organoberyllium species having a polymeric structure¹⁹.

(iii) From Organosodiums and -potassiums. Di- h^5 , h^1 -cyclopentadienylberyllium, is obtained by:

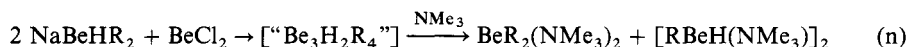


The pure product is isolated^{29,30} ($\leq 90\%$) from Et_2O after vacuum sublimation at $25^\circ\text{--}45^\circ\text{C}$. Benzene can be used as solvent, but although $\text{Be}(\text{C}_5\text{H}_5\text{-}h^5, \text{-}h^1)_2$ may react with THF, this latter solvent is also employed in its synthesis³¹. Using equimol BeCl_2 and $\text{Na}[\text{C}_5\text{H}_5]$, $h^5\text{-C}_5\text{H}_5\text{BeCl}$ ³² which can be purified by sublimation, is formed in ether. Mixed cyclopentadienylberyllium hydroborates are synthesized by^{33,34}:



Various bis(dienyl)beryllium compounds are obtained from 2:1 reactions of potassium dienide with BeCl_2 in THF at 40°C ^{35,36}; σ -bonded E-2,4-pentadienyl derivatives, $\text{Be}(\text{CHR}'\text{CR}'=\text{CR}''\text{CR}''=\text{CR}'''\text{H})_2(\text{L}_2)$ ($\text{R}, \text{R}', \dots = \text{H}$ or Me) form adducts, $\text{L} = \text{THF}$ (75–85% yield), and may be converted to complexes of N,N,N',N'-tetramethylethylenediamine (TMED), $\text{L}_2 = \text{TMED}$. Similarly prepared are bis(cyclooctadienyl)- and bis(cycloheptadienyl)beryllium³⁶.

Bimetallic, Na-containing reagents are involved in some preparations. Thus, BeMe_2 is the product of the interaction³⁷ of NaAlMe_4 and BeCl_2 in Et_2O .



Also, the two products of Me_3N are complexes that can be separated by fractional condensation because $\text{BeR}_2(\text{NMe}_3)$ is more volatile².

Bimetallic derivatives incorporating alkaline-earth metals are formed in equilibria:



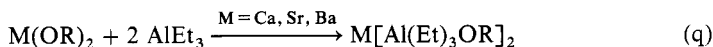
$\text{M} = \text{Ca}$ (70%), Sr (30%), Ba (40%)³⁸. Although the conversions are not quantitative, they are useful for $\text{M} = \text{Ca}$ or Sr because easy separation of products is achieved by dissolution in benzene. Complexes of formula $\text{BaHg}(\text{C}\equiv\text{CR})_4$ ($\text{R} = \text{H}, \text{Ph}$) are produced⁴ by reaction of $\text{Ba}(\text{NCS})_2$ with $\text{Hg}(\text{SCN})_2$ and $\text{KC}\equiv\text{CR}$ in liq NH_3 .

(iv) From Organoaluminums and -zincs. Aluminum and, especially, Zn are not effective in alkylating Be compounds. Equilibria are set up between trialkylaluminums and Be halides, e.g.³⁹:

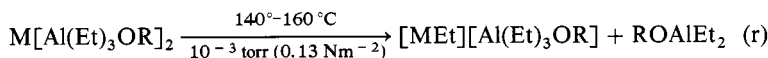


At low Al:Be ratios EtBeCl may be separated from such a mixture by distilling Et_2AlCl , removing other more soluble Al products and then extracting EtBeCl with toluene at 110°C . Further alkylation forming BeEt_2 occurs at higher Al:Be ratios or, alternatively, conversion of EtBeCl into BeEt_2 may be achieved by reduction with NaH and addition of the resulting EtBeH to ethene, (see §5.4.3.4.3); the BeEt_2 is distilled after the addition of electron-pair bases, such as quinoline, which form less volatile adducts with organoaluminums³⁹.

Complexes $\text{MX}_2 \cdot n \text{RAlX}_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{X} = \text{halide}$; $n = 1-4$) are synthesized⁴⁰ from MX_2 and RAlX_2 ; e.g., triethylaluminum combines with alkoxides of Ca, Sr or Ba to form bimetallic organometallic derivatives:



($\text{R} = \text{Et}, \text{n-Pr}, \text{n-Bu}$) which can undergo the further reactions³⁸:

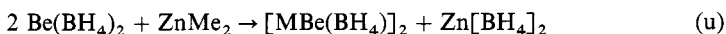


The ate complexes, $\text{M[AlEt}_4]_2$, can be separated from more volatile ROAlEt_2 and finally distilled in vacuo, $\text{M} = \text{Ca}$ (78%), Sr (55%), or recrystallized from benzene, $\text{M} = \text{Ba}$ (74.5%). A related reaction of BaH_2 is³⁸:



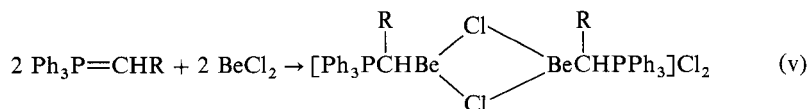
Beryllium hydride combines with complexes $\text{MAlR}_n\text{H}_{4-n}$ ($\text{M} = \text{Li}, \text{Na}$, $\text{R} = \text{hydrocarbyl}$, $n = 1-4$) to form⁴¹ species $\text{BeH}_2 \cdot \text{MAlR}_n\text{H}_{4-n}$.

Mixed methylberyllium hydroborates, e.g., $[\text{MeBe}(\text{BH}_4)]_2$, $[\text{MeBe}(\text{B}_3\text{H}_8)]_2$ and $\text{MeBeB}_5\text{H}_{10}$, are prepared in moderate to good yields by solvent-free reactions of Me_3Al or Me_2Zn :



From ZnMe_2 and $(\text{h}^5\text{-C}_5\text{H}_5)\text{BeB}_5\text{H}_8$ in the absence of solvent $(\text{h}^5\text{-C}_5\text{H}_5)\text{BeMe}$ forms⁴².

(v) From Alkylidenetriphenyl-phosphoranes or -arsoranes. Reactions in THF of 2:1 Ph_3PCHR with BeCl_2 , form the dimeric salts $[\text{Ph}_3\text{PCHBe}(\mu\text{-Cl})_2\text{BeCHRPPH}_3]\text{Cl}_2$ [$\text{R} = \text{H}$ (86.5%); $\text{R} = \text{Me}$ (36.0%)]⁴³ which are soluble in acidic solvents:



The As derivative is obtained (51%)⁴³ by using 1:1 Ph_3AsCH_2 and BeCl_2 .

(W. E. LINDSELL)

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5.4.3.3.2. by Redistribution with Its Diorganometallic Derivative.

Derivatives of formula $RBeX$ (X = halogen) are obtained from $^1 BeR_2$ and BeX_2 . Investigations using selective precipitation, molecular association and variable-T 1H NMR establish the existence of an equilibrium² when $M = Be$:



Rapid redistribution of R and X groups occurs between solvated, monomeric species of Eq. (a) in Et_2O at RT. The equilibrium lies to the right ($M = Be$; $X = Cl, Br$; $R = Me, Et, Ph$), so that Eq. (a) is a useful route to organoberyllium halides².

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5.4. Formation of Bonds between Elements

5.4.3. Formation of the Carbon—Group IIA-Element Bond

5.4.3.3. from Group-IIA Halides and Related Compounds

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5.4.3.3.2. by Redistribution with Its Diorganometallic Derivative.

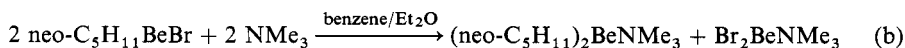
Derivatives of formula $RBeX$ ($X = \text{halogen}$) are obtained from $^1 BeR_2$ and BeX_2 . Investigations using selective precipitation, molecular association and variable- T 1H NMR establish the existence of an equilibrium² when $M = Be$:



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The $RBeX$ ($X = Cl$ or Br) compounds are prepared¹ from redistribution of 1:1 BeX_2 and BeR_2 in Et_2O when $R = Me, Et, t-Bu, neo-C_5H_{11}, Ph$. The products are monomeric in solution but may be isolated as solid etherates, e.g., $(t-BuXBe \cdot OEt_2)_2$ ($X = Cl, Br$)³, a halogen-bridged dimer. Addition of appropriate ligands to the ether solutions of $RBeX$ gives complexes, including $RXBe \cdot \text{dioxane}$ ($R = Me, X = Cl, Br$; $R = Ph, X = Cl$)²,

$\text{EtClBe} \cdot \text{bipy}^4$ and monomeric $\text{RBrBe} \cdot \text{TMED}$ (tetramethylethylenediamine; $\text{R} = \text{Et}$, $\text{neo-C}_5\text{H}_{11}$)⁵, but addition of NMe_3 to $\text{neo-C}_5\text{H}_{11}\text{BeBr}$ causes redistribution⁵:



No reaction occurs between BeMe_2 and BeCl_2 in the absence of solvent at 140°C during 1 h⁶, but stirring freshly sublimed BeCl_2 with 3–4 mol xs BeEt_2 at RT (12 h) followed by further reaction (24 h) in cyclohexane gives unsolvated, polymeric EtBeCl quantitatively⁷. Unsolvated t-BuBeCl may be obtained by stirring BeCl_2 and $\text{Be}(\text{Bu-t})_2$ in benzene (24 h)⁸; the product may be isolated by sublimation [$120^\circ\text{--}130^\circ\text{C}$, 10^{-3} torr, 70–80%] and it forms a 1:1 adduct with quinuclidine, $\text{t-BuClBe} \cdot \text{NC}_7\text{H}_{13}$.

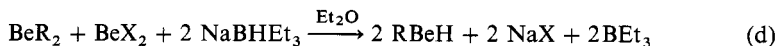
The unsolvated cyclopentadienyl derivatives $\text{h}^5\text{-C}_5\text{H}_5\text{BeX}$ ($\text{X} = \text{Cl}$, Br , I) are prepared by redistribution of the binary compounds [see Eq. (a)] at 50°C in the absence of solvent⁶ and isolated and purified by volatilization in vacuo. Stirring $\text{Be}(\text{C}_5\text{H}_5\text{-h}^5, \text{h}^1)_2$ in ether with anhydrous FeBr_2 at -78°C to RT for 2 h forms⁹ volatile $\text{h}^5\text{-C}_5\text{H}_5\text{BeBr}$ which is separated by sublimation [RT; 10^{-1} torr (13 Nm^{-2})] from $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Fe}$ and unreacted $\text{Be}(\text{C}_5\text{H}_5\text{-h}^5, \text{h}^1)_2$.

The redistribution of Eq. (a) is not used for preparation of organoalkaline-earth metal halides, $\text{M} = \text{Ca}$, Sr , Ba . Nevertheless, such an equilibrium exists when $\text{M} = \text{Ca}$, and the poor solubility of CaX_2 ($\text{X} = \text{halide}$) promotes formation of CaR_2 in Et_2O and even in THF^{10,11}.

Hydrides, RBeH , may be prepared by combining redistribution and reduction in a single step ($\text{X} = \text{Cl}$ or Br)^{1,12}:



Using BeBr_2 in refluxing Et_2O , the products RBeH ($\text{R} = \text{Me}$, Et , Ph) are obtained as etherates in 70–80% yield. Attempts to desolvate $(\text{MeHBe} \cdot \text{OEt}_2)_2$ at $50^\circ\text{--}70^\circ\text{C}$ lead to decomposition after loss of ca. 83% of coordinated Et_2O ; thermal disproportionation of MeBeH into BeMe_2 and a hydride-rich residue occurs, especially at $170^\circ\text{--}210^\circ\text{C}$ ¹³. Addition of TMED to benzene–ether solutions of RBeH produces $(\text{RBeH})_2 \cdot \text{TMED}$. When $\text{R} = \text{Ph}$ reaction (c) is slow if $\text{X} = \text{Br}$, and RBeH is not formed when $\text{R} = \text{t-Bu}$, $\text{X} = \text{Br}$. Reduction with LiH proceeds better with BeCl_2 , and, using reaction (c) ($\text{X} = \text{Cl}$), the hydrides RBeH ($\text{R} = \text{t-Bu}$, $\text{n-C}_5\text{H}_{11}$, Ph , o-tolyl) are obtained as TMED adducts¹⁰. Alternatively, PhBeH is formed in 1 h at RT using ($\text{X} = \text{Cl}$)¹⁴:



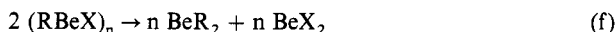
and $(\text{neo-C}_5\text{H}_{11}\text{BeH})_2 \cdot \text{TMED}$ is obtained similarly⁵.

Redistribution of BeR_2 with BeH_2 in toluene at $50^\circ\text{--}55^\circ\text{C}$ forms the polymeric product RBeH :

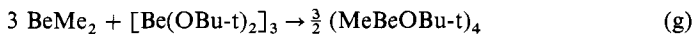


for $\text{R} = \text{Me}$, Et and similarly for $\text{R} = \text{Ph}$ ¹³. In the absence of solvent at $105^\circ\text{--}115^\circ\text{C}$, reaction (e) ($\text{R} = \text{C}_5\text{H}_5$) yields¹⁰ $\text{h}^5\text{-C}_5\text{H}_5\text{BeH}$, which is soluble in hydrocarbons and may be isolated using pet. ether. Purification by distillation is possible, but thermal decomposition occurs at higher T ¹⁶.

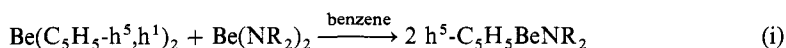
The $(\text{RBeX})_n$ ($\text{X} = \text{OR}$, $n = 2\text{--}4$; $\text{X} = \text{SR}$, $n = 4$; $\text{X} = \text{NR}_2$, $n = 2, 3$) derivatives are not produced by redistribution. Disproportionation is more often observed, especially in the presence of pyridine (py) and related ligands¹:



Species $[\text{RBe}(\text{OR}')_n]$ are more stable to disproportionation than $(\text{RBeSR}')_n$; e.g., $[\text{MeBe}(\text{OMe})_4]$ disproportionates only in the presence of 2,2'-bipyridyl or 4 equiv py but forms an adduct $\text{Me}(\text{OMe})\text{Be}\cdot\text{py}$, with xs py, as also does the t-butoxide, $(\text{MeO}-t\text{-BuBe}\cdot 2\text{ py})$; $(\text{RBeSBu-t})_4$ disproportionates on dissolution in benzene at RT ($\text{R} = \text{Me}$) or 50°C ($\text{R} = \text{Et}$). However, variation in R and X groups can modify the relative stabilities of compounds and redistribution can occur, e.g.¹:



Variation in stabilities of dialkylamido compounds are also observed; $(\text{MeBeNMe}_2)_3$ forms a stable py adduct, but $(\text{MeBeNPr-n}_2)_2$ disproportionates on py addition¹. A good method for preparing $\text{h}^5\text{-C}_5\text{H}_5\text{BeNR}_2$ ($\text{R} = \text{Me, Et}$) is¹⁷:



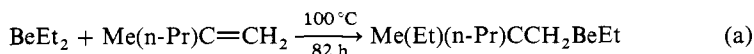
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5.4.3.4. from Other Group-IIA Organometallics of the Same Metal

5.4.3.4.1. by Addition to Olefinic or Acetylenic Derivatives.

(i) Be. The few additions of organoberyllium compounds to unsaturated carbon—carbon bonds are similar to those of organoaluminums. With 1,1-dialkylated ethene, simple addition occurs and reaction in a sealed tube proceeds to high conversion¹:



Further alkene insertion into the β -substituted alkylberyllium bond is not observed, and the resulting alkyl group is also stabilized to β -hydrogen elimination. Higher alkylberyl-

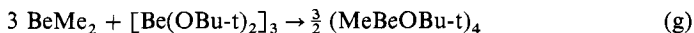
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5.4. Formation of Bonds between Elements

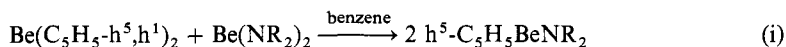
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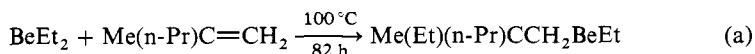
(W. E. LINDSELL)

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5.4.3.4. from Other Group-IIA Organometallics of the Same Metal

5.4.3.4.1. by Addition to Olefinic or Acetylenic Derivatives.

(i) Be. The few additions of organoberyllium compounds to unsaturated carbon—carbon bonds are similar to those of organoaluminums. With 1,1-dialkylated ethene, simple addition occurs and reaction in a sealed tube proceeds to high conversion¹:

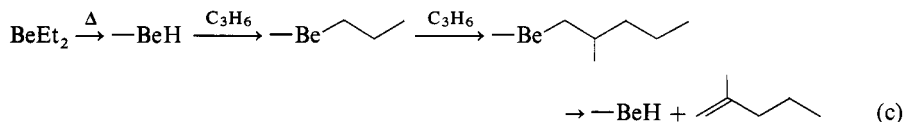


Further alkene insertion into the β -substituted alkylberyllium bond is not observed, and the resulting alkyl group is also stabilized to β -hydrogen elimination. Higher alkylberyl-

lithium compounds with β -hydrogens are susceptible to thermal decomposition into metal hydride and alkene²:

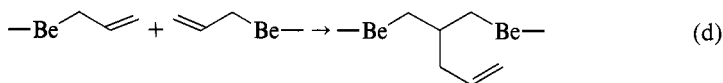


Propene at 200 atm ($2 \times 10^4 \text{ Nm}^{-2}$) and other straight-chain 1-alkenes undergo catalytic dimerization in the presence of BeEt_2 at $200^\circ\text{--}350^\circ\text{C}$ ³. A hydride is probably involved in the first stage, followed by addition of organometallic to alkene, giving a β -substituted derivative that undergoes hydride elimination more readily than further insertion:



Ethene at 110–160 atm ($1.1\text{--}1.6 \times 10^4 \text{ Nm}^{-2}$) and $60^\circ\text{--}80^\circ\text{C}$ is polymerized by BeEt_2 by a series of addition steps. Other ethene polymerization activators include⁴ BePh_2 and NaBeEt_3 . Organoberyllium compounds are also components of various mixed systems, related to typical Ti–Al catalysts for vinyl polymerizations².

Diallylberyllium tends to undergo oligomerization by such additions as:

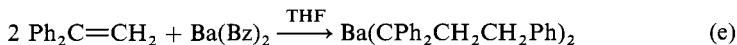


and further reaction is also observed to form bridging organic groups with 9, 12, etc., carbon atoms⁵.

Diorganoberylliums, BeR_2 , are claimed to react with alkynes, $\text{R}'\text{C}\equiv\text{CR}'$, giving both the simple addition product $\text{cis-RR}'\text{C}=\text{CHR}'$ on hydrolysis and also the coupled product⁶ $\text{R}'\text{CH}=\text{CR}'\text{CR}'=\text{CHR}'$; however, Et_2BeL ($\text{L} = \text{TMED}$ or NMe_3) is unreactive to 2-butyne at 70°C ⁷.

(ii) Ca, Sr and Ba. The main application of the addition of organometallics of the heavy alkaline-earth metals to alkenes is in the initiation and propagation of vinyl polymerization and not in the formation of discrete, isolable compounds with M—C bonds^{8–10}.

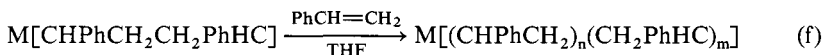
Diorganoderivatives, MR_2 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$), are alkene and diene polymerization initiators. An initiator, $\text{Ba}(\text{CPh}_2\text{CH}_2\text{CH}_2\text{Ph})_2$, is formed from dibenzylbarium¹¹:



This product is obtained in high yield; tetrahydrofuran (THF) may be removed in vacuo. In THF *xs* 4,4'-bis(1-phenylethylene)-1,1'-biphenyl (BPB) reacts rapidly with $\text{Ba}(\text{CMe}_2\text{Ph})_2$ to form a monoadduct $\text{Ba}(\text{PhMe}_2\text{CCH}_2\text{CPhC}_6\text{H}_4\text{CPh}=\text{CH}_2)_2$ which contains a monoanionic organic group¹²; a similar addition of polystyrylbarium to BPB occurs. If *xs* organobarium is employed a second, slow addition to the residual double bond occurs to form bianionic $\text{Ba}[\text{RCH}_2\text{CPhC}_6\text{H}_4\text{CPhCH}_2\text{R}]$ ($\text{R} = \text{CMe}_2\text{Ph}$ or polystyryl). Reaction of $\text{Ba}(\text{Bz})_2$ with a 3.5-fold *xs* α -methylstyrene in THF yields a living oligomer, $\text{Ba}[\text{C}(\text{Ph})\text{MeCH}_2(\text{CPhMeCH}_2)_n\text{CH}_2\text{Ph}]_2$ ($n \approx 2\text{--}4$), in $\leq 95\%$ conversion¹³. Similar oligomeric species are formed by interaction of finely divided Ba metal with α -methylstyrene^{14,15}. These oligomeric products are bianionic derivatives formed by radical coupling of the initial radical anion followed by addition to alkene, $\text{Ba}[(\text{CPhMeCH}_2)_n(\text{CH}_2\text{PhMeC})_m]$ ($m \geq 1, n \geq 1$), but monoanionic organic groups,

including $[\text{CMePhCH}_2\text{C(Ph)Me}_2]^-$, also arise from hydrogen transfer processes promoted by higher concentrations of reactants and longer times.

Bicarbanionic oligostyrylbarium and-strontium are prepared by reaction of styrene with finely divided metal in THF or tetrahydropyran¹⁶. Initial electron transfer and radical coupling is followed by insertion:



(M = Sr, Ba); the best T for reaction is 30°–40 °C and dimers, trimers and tetramers are obtained using dilute solutions. Unlike α -methylstyrene, deactivation of bicarbanionic ends does not take place, but aging in THF by protonation from solvent occurs in a nonrandom process in which both ends of the living oligomer are deactivated so that no monocarbanions are formed¹⁷. Anionic polymerization of styrene is accomplished by MR_2 compounds (M = Ba, Sr, Ca)^{8,9}; in particular for initiators $\text{Ba}[\text{CPh}_2\text{CH}_2\text{CH}_2\text{Ph}_2\text{C}]$ ¹⁸, $\text{Ba}[\text{Bz}]_2$ ¹⁹, $\text{Ba}[\text{CPh}_3]_2$ ²⁰, oligo- α -methylstyrene-barium^{13–15}, $\text{Ba}[\text{CPh}_2\text{CH}_2\text{CH}_2\text{Ph}]_2$ ¹¹ and the free metals^{8,17}. In comparison with $\text{Ba}(\text{Bz})_2$ the more ionic derivative, $\text{Ba}(\text{CPh}_3)_2$, initiates more slowly, and the presence of bulky CPh_3 groups at the growing end causes slow propagation and chain transfer²⁰.

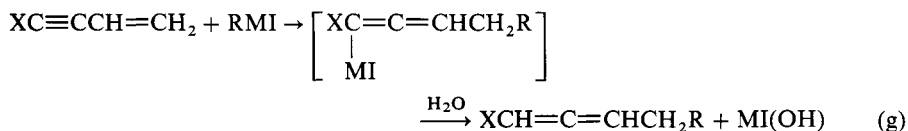
Living polymers of conjugated diene molecules, especially butadiene and isoprene, are produced by addition using MR_2 initiators (M = Ca, Sr, Ba). Polymerizations by $\text{M}[\text{CPh}_2\text{CH}_2\text{CH}_2\text{Ph}_2\text{C}]$ (M = Sr²¹, Ba^{18,22}), $\text{M}[\text{Bz}]_2$ (M = Sr²³, Ba¹⁹), $\text{Ba}[\text{CPh}_3]_2$ ²⁰, oligo- α -methylstyrylbarium¹⁵ and the finely divided metals^{8–10} occur. Barium-promoted polymerization of butadiene in hydrocarbons such as benzene affords polymer with ca. 70 % cis-1,4 microstructure, whereas Sr or Ca compounds give mainly trans-1,4-polybutadiene²¹. In THF ≤ 80 % 1,4-polybutadiene, with trans addition in xs, is formed by Ba or Sr initiators; 1,2 linkages are formed in the more polar solvent, 1,2-dimethoxyethane (DME)^{18,21} where there is a long induction prior to polymerization²².

Anionic polymerization of 4-vinylpyridine by $\text{Ba}[\text{CMe}_2\text{Ph}]_2$ occurs in THF, giving a non-stereospecific polymer; 2-vinylpyridine is also polymerized by $\text{Ba}[\text{CMe}_2\text{Ph}]_2$ or difunctional initiator $\text{Ba}[\text{Ph}_2\text{CCH}_2\text{CH}_2\text{CPh}_2]$, giving > 50 % isotactic linkages²⁴.

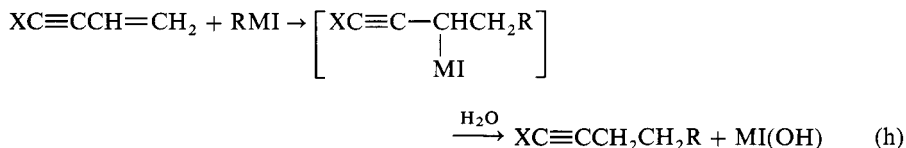
Methylmethacrylate is polymerized by MR_2 compounds. In DME syndiotactic polymer (89 %) is produced by diindenylcalcium, but diphenylcalcium forms a polymer with more isotactic sequences and isotacticity is increased by the use of less polar solvents²⁵.

Organometallics RMX (M = Ca, Sr, Ba; X = halogen) participate in polymerization and in additions to conjugated vinylacetylenes^{8,26}. These organometallics exist in equilibrium with MR_2 species in solution and may often be halogen deficient, so that reactions of the diorganometals must also be considered. Cyclohexene does not react with MeCaI after 60 h at 20 °C²⁷. 1,1-Diphenylethene in THF gives a dark red coloration with MeCaI , but after 60 h at 20 °C the yield of addition product, $(\text{EtPh}_2\text{C})\text{CaI}$, is negligible²⁷.

Addition of compounds RMI (R = alkyl, aryl; M = Ca, Ba) to terminal vinylacetylenes occurs exothermically in Et_2O at $\leq \text{RT}$ ^{8,26,28}. The initial organometallics are not isolated or structurally identified, but the products of hydrolysis are obtained in varying yields, 15–70 %, and may be the result of overall 1,4:



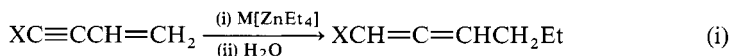
or 1,2 addition:



The 1,4 product is formed exclusively when X is a carbon substituent, e.g., X = alkyl, aryl, vinyl, $\text{Me}_2\text{C(OH)}$, Me_2NCH_2 and also X = SR; the allenic organometallic of Eq. (g) is an intermediate. When X = SiMe_3 or GeEt_3 both 1,4 and 1,2 products are isolated in ca. 1:1 ratio. The products here arise from hydrolysis of either of the two isomeric forms of the intermediate organometallic [see Eqs. (g) and (h)], or of a common intermediate in dynamic equilibrium between these forms.

Conjugated dienes are polymerized by n-BuCaI (in admixture with n-Bu₂Ca) by a typical anionic addition mechanism at 20°–50°C²⁹. Initiation by addition is slow compared to the subsequent polymerization, and the microstructure of the polymer is solvent dependent. Polybutadiene with predominantly trans-1,4 links (48–72%) is obtained in hydrocarbons or Et₂O, but 1,2-polymerization is promoted in THF or by addition of hexamethylphosphoramide (HMPA). Polymerization of butadiene by Ph_3CMX (M = Ca, Sr, Ba; X = Cl, Br) at –10°C in THF yields polymer with increasing 1,4- content M = Ca < Sr < Ba; Ph_3CBaCl produces 36% trans-1,4, 45% cis-1,4 and 19% 1,2-linkages³⁰. Styrene is polymerized by n-BuCaI²⁹ and Ph_3CMX (M = Ca, Sr, Ba)³⁰ which also polymerizes 2- and 4-vinylpyridine. Polymethylmethacrylate is obtained in high yield using Ph_3CMX initiators (M = Ca, Sr, Ba; X = Cl, Br), and the tacticity of the polymer varies with metal, solvent and halide³¹.

Bimetallic compounds $\text{M}[\text{ZnR}_4]$ (M = Ca, Sr, Ba) are formed by reaction of alkaline-earth metals with diorganozincs but are sometimes described as MR_2 derivatives⁸. The $\text{M}[\text{ZnEt}_4]$ derivatives react with 1,1-diphenylethene in refluxing benzene or benzene-ether to give the addition compound characterized as the acid $\text{C}_3\text{H}_7(\text{Ph})_2\text{CCOOH}$ after carbonation (M = Sr, 20%; M = Ba, 21.6%)³². The organometallic product must be a bimetallic complex of bis(1,1-diphenylbutyl) metal and Et₂Zn. Compounds described as MEt_2 but actually zincates, $\text{M}[\text{ZnEt}_4]$ (M = Ca, Sr, Ba), add to terminal vinylacetylenes in Et₂O at RT to form organometallics^{8,26,33}. These organometallics are probably ate complexes and yield allenes on hydrolysis:



where if M = Ca, X = alkyl, phenyl, vinyl; if M = Sr, R = alkyl; if M = Ba, X = alkyl, vinyl, RS, R₂NCH₂.

The $\text{M}[\text{ZnR}_4]$ and $\text{M}[\text{AlR}_4]_2$ ate complexes (M = Ca, Sr, Ba) polymerize vinyl and conjugated diene monomers including styrene, methylmethacrylate, acrylonitrile, vinylketones, isoprene and butadiene^{8,34,35}. The bimetallic complexes produce polymers of differing microstructure to that formed by simple alkaline-earth metal initiators, so that the presence of Zn or Al influences the stereochemistry of propagation. Thus, polybutadiene obtained in benzene from a Ba–Zn initiator contains more than 90% 1,4-bonds (trans-1,4: 75–81%)³⁴.

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5.4.3.4.2. with Acidic Hydrocarbons to Evolve RH.

(i) Be. Synthesis of organoberylliums by metal-hydrogen exchange of acidic hydrocarbons is uncommon. Reaction of $\text{PhC}\equiv\text{CH}$ with $\text{Et}_2\text{Be}\cdot\text{TMED}$ (tetramethyl-

5.4. Formation of Bonds between Elements

5.4.3. Formation of the Carbon—Group IIA-Element Bond

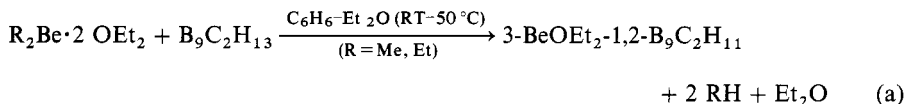
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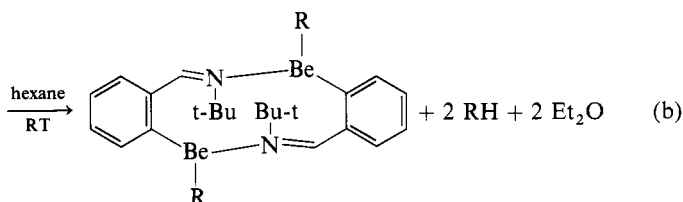
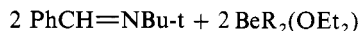
(i) **Be.** Synthesis of organoberylliums by metal-hydrogen exchange of acidic hydrocarbons is uncommon. Reaction of $\text{PhC}\equiv\text{CH}$ with $\text{Et}_2\text{Be}\cdot\text{TMED}$ (tetramethyl-

ethylenediamine) to form $\text{Be}(\text{C}\equiv\text{CPh})_2$ (69%) is slow (24 days, 80°C), and related metallations of 1-alkynes may be complicated by side reactions including addition¹. A special example is the formation of 3-beryllio-1,2-dicarba-closo-dodecarborane²:



The crystalline product is obtained as an ether adduct on removal of solvent. The Be atom is incorporated into the icosahedral structure and connected to two carbon and three Be atoms. The coordinated ether may be displaced by NMe_3 , but the ether-free derivative is polymeric.

Although some organoberylliums add to $\text{C}=\text{N}$ bonds, an unusual reaction is the o-metallation:

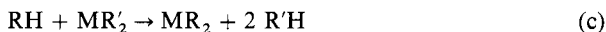


($\text{R} = \text{Et}$, t-Bu ; 50%)³. The yellow-orange crystalline product is a dimer when $\text{R} = \text{Et}$ but exists in a dimer-monomer equilibrium in benzene when $\text{R} = \text{t-Bu}$.

The bimetallic complex $(\text{K}[\text{BeEt}_2\text{OBu-t}])_2$ metallates boiling toluene to give a red crystalline product of empirical formula $\text{K}_5\text{Be}_3\text{Et}_3(\text{OBu-t})_4(\text{CH}_2\text{Ph})_4$ in low yield; with boiling mesitylene metallation occurs at aromatic $\text{C}-\text{H}$ and red crystals of empirical formula $\text{K}_3\text{Be}_2\text{Et}_2(\text{OBu-t})_2(\text{mesityl})_2$ are formed in higher yield⁴.

(ii) Ca , Sr and Ba . Reactions of organometallics of Ca , Sr and Ba with hydrocarbons yield MR_2 , RMX ($\text{X} = \text{halogen}$) or bimetallic ate complexes with Zn or Al ⁵. Metallation can occur to high conversion in an ether (see Table 1) provided that the pK_a of the organic compound RH is less than that of the conjugate acid of the organic ligand in MR'_2 or $\text{R}'\text{MX}$. Hydrocarbons RH that react are cyclopentadiene, indene, fluorene, 1-alkynes and triphenylmethane. Metallation to lower conversion occurs with diphenylmethane, pentafluorobenzene, anisole and some heterocyclic aromatics (see Table 1).

Compounds MR'_2 form diorganometal derivatives:



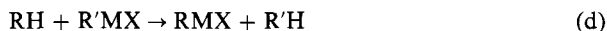
but the intermediate mixed species, $\text{MR}'\text{R}$, is not isolated. Diorganometal reagents that are synthesized easily and prove useful for metallation are CaPh_2 (prepared from Ca metal and HgPh_2)⁶, $\text{M}(\text{CPh}_2\text{CH}_2\text{CH}_2\text{Ph}_2\text{C})$ ($\text{M} = \text{Sr}$, Ca ; prepared from the metal and $\text{Ph}_2\text{C}=\text{CH}_2$)⁷ and $\text{Ba}(\text{CMe}_2\text{Ph})_2$ (prepared from PhCMe_2OMe and Ba metal)⁸ (see Table 1). Cyclopentadiene reacts with $\text{Ca}(\text{C}\equiv\text{CPh})_2$ to form $\text{Ca}(\text{C}_5\text{H}_5\text{-h}^1)_2$ in high yield in boiling tetrahydrofuran (THF)⁹, even though the pK_a of C_5H_6 and $\text{PhC}\equiv\text{CH}$ are relatively close, ca. 15 and 18.5, respectively. Other MR'_2 ($\text{M} = \text{Ca}$, Sr , Ba) are claimed¹⁰ as effective metallating agents of acidic hydrocarbons, including indene in THF.

TABLE 1. PREPARATION OF ORGANOCALCIUMS, -STRONTIUMS AND -BARIUMS BY METALLATION OF RH

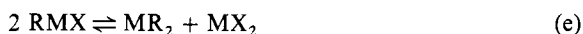
RH	Metallating agent	Solvent (T °C)	Product (yield, %)	Ref.
Cyclopentadiene	MeCaI	THF (60)	(h ¹ -C ₅ H ₅)ICa·2 THF (40)	12
Indene	Ca[C ₂ Ph] ₂	THF (reflux)	Ca(C ₃ H ₅) ₂ (80)	8
	MeCaI	THF (−30)	C ₉ H ₇ CaI (99)	13
	Ph ₃ CCaCl	THF (−20)	(C ₉ H ₇) ₂ Ca·2 THF (65)	11
	Ca[AlEt ₄] ₂	n-alkane (100–150)	C ₉ H ₇ Ca[AlEt ₄] (90–96)	20
Fluorene	MeCaI	THF (−30)	C ₁₃ H ₉ CaI (93)	13
	Ph ₃ CCaCl	THF (RT)	C ₁₃ H ₉ CaCl·2 THF (88)	11
	CaPh ₂	THF (RT)	Ca(C ₁₃ H ₉) ₂ ·2 THF (70)	6
	PhSrI·0.5 TMED ^a	THF (20)	C ₁₃ H ₉ SrI·0.5 THF (45.1)	17
	[M(CPh ₂ CH ₂ CH ₂ Ph ₂ C)] (M = Sr, Ba)	THF (RT)	M(C ₁₃ H ₉) ₂	7
RC≡CH (R = alkyl, Ph)	PhCaI	Et ₂ O	RC≡CCaI (46–91)	15
PhC≡CH	Ph ₃ CCaCl	THF (RT)	PhC≡CCaCl·x THF	11
	M[ZnEt ₄] (M = Ca, Sr, Ba)	Et ₂ O (≤ RT)	M(C ₂ Ph) ₂ ·ZnEt ₂	19
Ph ₃ CH	I(Ph)CaDABCO ^c	Et ₂ O-THF (RT)	Ph ₃ CCaI (14.5)	18
	CaPh ₂	THF (RT)	Ca(CPh ₃) ₂ ·THF (72)	6
	Ba(CMe ₂ Ph) ₂	THF(15)	Ba(CPh ₃) ₂	8
Ph ₂ CH ₂	CaPh ₂	THF (RT)	Ca(CHPh ₂) ₂ (20.2)	6
C ₆ F ₅ H	(Ph)ICaDABCO ^b	Et ₂ O-THF (−20)	C ₆ F ₅ CaI (22.1)	18
C ₆ H ₅ OMe	PhCaI	THF (RT)	(o-MeOC ₆ H ₄)CaI (16)	14
Thiophene	MeCaI	THF (RT)	2-(ICa)C ₄ H ₃ S (21)	14
Dibenzofuran	PhCaI	Et ₂ O (reflux)	4-(ICa)C ₁₂ H ₇ O (3.7)	16
Dibenzothiophene	PhCaI	Et ₂ O (reflux)	3-(ICa)C ₁₂ H ₇ S (~9)	15
9-Ethylcarbazole	PhCaI	Et ₂ O (reflux)	1-(ICa)C ₁₂ H ₇ NC ₂ H ₅ (<15)	16

^a TMED = N,N,N',N'-tetramethylethylenediamine.^b DABCO = 1,4-diazabicyclo[2.2.2]octane.

Metallating agents R'MI form the organometal iodides (X = I):



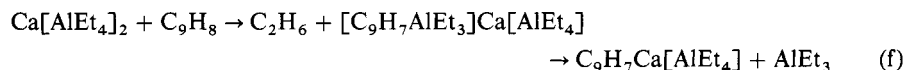
although the products are not always isolated from solution. On the other hand, metallation of cyclopentadiene or indene by Ph₃CCaCl in THF yields only the soluble derivatives CaR₂ (R = C₅H₅, C₉H₇), whereas fluorene or diphenylacetylene form the sparingly soluble RCaI (R = C₁₃H₉, PhC≡C)¹¹. These differences reflect the relative insolubilities of RCaX, CaR₂ and CaX₂ and the existence of an equilibrium:



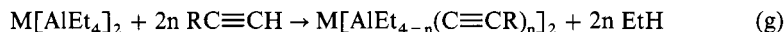
When first formed CaI_2 is soluble in THF and the solubility of the $\text{I}_2\text{Ca}\cdot\text{THF}$ complex is 0.8 mol dm^{-3} at 20°C , but only $7 \times 10^{-3} \text{ mol dm}^{-3}$ at 0°C ¹². Compounds RCaI ($\text{R} = \text{Me}^{12-14}$, $\text{Ph}^{15,16}$), PhSrI ¹⁷ and Ph_3CCaCl ¹¹ are prepared by direct reaction of the metal with organic halide and their reactions with acidic hydrocarbons, RH , are given in Table 1. Although active with $\text{PhC}\equiv\text{CH}$ ¹⁵, solutions of PhMI ($\text{M} = \text{Ca}, \text{Sr}$) are poor metallating agents; the $\text{PhCaI}\cdot\text{L}$ complexes [$\text{L} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$, TMED]¹⁸ or $\text{PhSrI}\cdot 0.5 \text{ TMED}$ ¹⁷ are more active (see Table 1). Metallation of anisole, dibenzofuran, 9-ethylcarbazole and dibenzothiophene by unactivated PhCaI only proceeds to low conversion, but the formation of 3-(iodocalcio)dibenzothiophene is unusual¹⁶.

The $\text{M}[\text{ZnEt}_4]$ derivatives ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) react with 2 mol $\text{PhC}\equiv\text{CH}$ to give $\text{M}(\text{C}\equiv\text{CPh})_2$ mixed with ZnEt_2 , probably as an ate complex¹⁹. However, $\text{M}[\text{ZnEt}_4]$ complexes are less active in Et_2O than PhCaI toward anisole, dibenzofuran and dibenzothiophene [e.g., from the latter substrate 4-metallated dibenzothiophene is obtained in $<1\%$ yield ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$)⁵].

Reaction of the $\text{Ca}[\text{AlEt}_4]_2$ ate complex with 1 equiv indene in $n\text{-C}_8\text{H}_{18}$, $n\text{-C}_{10}\text{H}_{22}$ or $n\text{-C}_{12}\text{H}_{26}$ occurs in 90–96% conversion²⁰:



The complexes $\text{M}[\text{AlEt}_4]_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) react with alkynes, $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{alkyl}, \text{Ph}$), in hydrocarbons at $\leq 200^\circ\text{C}$ ²¹:



The values of $n = 1, 2$ or 3 are determined by reaction conditions, and reactivity increases as $\text{M} = \text{Ca} < \text{Sr} < \text{Ba}$. Mixtures of products may result, but characterized complexes are $\text{M}[\text{AlEt}(\text{C}\equiv\text{CPh})_3]_2$ ($\text{M} = \text{Ca}, 95.5\%$; $\text{Sr}, 96.5\%$; $\text{Ba}, 92.0\%$) and $\text{Ca}[\text{AlEt}_2(\text{C}\equiv\text{CR})_2]_2$ ($\text{R} = \text{C}_4\text{H}_9, 90\%$; $\text{C}_5\text{H}_{11}, 95\%$)²¹.

Reaction of CaC_2 with cyclopentadiene in liq NH_3 , decalin- liq NH_3 or ethylenediamine forms $\text{Ca}(\text{C}_5\text{H}_5)_2$ and acetylene²²; $\text{M}(\text{C}_5\text{H}_5)_2$ is formed in low yields from C_5H_6 and MH_2 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) at 400°C ⁵ and metallation of C_5H_6 , C_9H_8 and malonic ester with $\text{Ca}(\text{NH}_2)_2$ in liq NH_3 ²³ may also be noted.

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5.4.3.4.3. by Transfer of Metal Hydride to Olefinic or Acetylenic Derivatives.

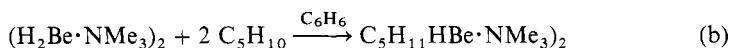
Organoberyllium hydrides, RBeH , are obtained as solvated products by reduction in ether of RBeX ($\text{X} = \text{Cl}, \text{Br}$) using LiH or $\text{Na}[\text{BHEt}_3]$ and by exchange between BeR_2 and Et_3SnH in solution¹. Base-free compounds, RBeH , are formed on pyrolysis of some R_2Be , especially RBeBu-t^2 , or by redistribution between BeR_2 and BeH_2 (see §5.4.3.3.2). These hydrides resemble related Al and boron derivatives in their ability to hydrometallate olefinic bonds¹.

Ethene ($<100 \text{ Nm}^{-2}$) reacts with $\text{RBeH} \cdot n \text{ OEt}_2$ ($\text{R} = \text{Me}, \text{Et}; n < 1$) or $(\text{EtHBe} \cdot \text{NMe}_3)_2$ in a sealed tube at 84°C in the absence of solvent:



Reaction is extensive after 2 h and complete in 8 h³. (Some symmetrization of alkyl groups may occur when $\text{R} = \text{Me}$.) The reactivity is not markedly altered by the presence of Et_2O or Me_3N ; however, $\text{Na}[\text{BeHEt}_2]$ adds readily to ethene ($<100 \text{ Nm}^{-2}$, 8 h, 84°C) in the presence of Et_2O , but slowly in its absence³. Reaction of ethene ($5\text{--}8 \times 10^2 \text{ Nm}^{-2}$, $65^\circ\text{--}70^\circ\text{C}$, 2–10 h) with EtBeH , formed in situ by reduction with NaH of the product of redistribution between BeCl_2 and AlEt_3 , is a preparative route⁴ to BeEt_2 .

Higher terminal alkenes, specifically 1-pentene and 1-decene, react with RBeH . The relative rates for reaction of 1-pentene with equimolar RBeH , ascertained by ^1H NMR in benzene, are illustrated in Table 1; reaction half-lives using base-free $i\text{-BuBeH}$, $(i\text{-BuHBe} \cdot \text{OEt}_2)_2$ or $(i\text{-BuHBe} \cdot \text{NMe}_3)_2$ are in the ratio 1:40:110, respectively⁵. Negligible reaction takes place within 160 h at 84°C between 1-pentene and binary BeH_2 [formed from $\text{Be}(\text{BH}_4)_2$ and PPh_3], but when EtBeH is added, reaction is complete under the same conditions³. Moreover, the discrete complex $(\text{H}_2\text{Be} \cdot \text{NMe}_3)_2$ containing both terminal and bridging hydrogen atoms reacts with 1-pentene at a rate similar to the hydrogen bridged complex $(i\text{-BuHBe} \cdot \text{NMe}_3)_2$:



(see Table 1)⁶. Thus higher reactivity cannot be ascribed solely to the presence of terminal Be-H groups. The activation energy of $67 \pm 8 \text{ kJ mol}^{-1}$ for addition of $(\text{MeHBe} \cdot \text{NMe}_3)_2$ to 1-decene supports a preliminary dissociation into monomeric $\text{MeHBe} \cdot \text{NMe}_3$ prior to reaction¹.

5.4. Formation of Bonds between Elements

5.4.3. Formation of the Carbon—Group IIA—Element Bond

5.4.3.4. from Other Group-IIA Organometallics of the Same Metal

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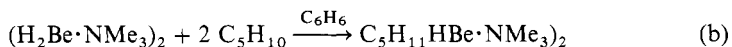
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TABLE 1. REACTION CONDITIONS FOR 1:1 ADDITION OF ALKYLBERYLLIUM HYDRIDES TO ALKENE

Alkene	Reagent ^a	T (°C)	Half-life of alkene (h)	Ref.
1-Pentene	EtHBe·n OEt ₂	50	0.4	3
	EtHBe·n OEt ₂	33.5	4.85	3
	i-BuBeH	33.5	~0.2	5
	(i-BuHBe·OEt ₂) ₂	33.5	7-9	5
	(i-BuHBe·NMe ₃) ₂	33.5	20-25	5
	(H ₂ Be·NMe ₃) ₂	33.5	25	6
2-Pentene (95% cis)	EtHBe·n OEt ₂	50	≈ 90	3
2-Methylbut-2-ene	EtHBe·n OEt ₂	84	no reaction	3
	i-BuBeH	110	50	5

^a Benzene also present.

Internal alkenes react less readily with RBeH. The reactivity of 1-pentene to EtHBe·n OEt₂ is >200 times that of 2-pentene; the trialkylated ethene, 2-methylbut-2-ene, is inactive to addition of RBeH (R = Et, i-Bu) at 84°C and reacts only slowly with the more active, base-free i-BuBeH at 110°C (see Table 1)^{3,5}. Beryllium migrates to the end of the carbon chain as shown by the bromination of the products from 2-pentene and EtBeH: 82% 1-bromopentane, 12% 2-bromopentane and 6% 3-bromopentane³.

Thermal isomerization of t-Bu₂Be to i-Bu₂Be, which occurs slowly even at RT, proceeds by elimination and recombination by hydrometallation of 2-methylpropene with an intermediate beryllium hydride¹; a similar mechanism accounts for the racemization of (+)-Be[(R)—CH₂CH(Me)Et]₂.

Reactions of alkylberyllium hydrides with internal acetylenes, RC≡CR, are complex and involve both Be—H and Be—C addition to the acetylenic bond^{1,8}.

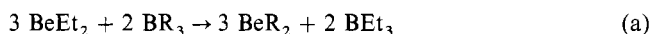
The hydrides MH₂ (M = Ca, Sr, Ba), suspended in organic solvents, react with alkenes (e.g., propene, 4 × 10⁻⁴ Nm⁻², 90°C in toluene, M = Ca) in the presence of suitable catalysts (e.g., AlEt₃) to form alkylmetal compounds⁹.

(W. E. LINDSELL)

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5.4.3.4.4. by Reaction with other Organometallics.

The exchange of organic groups between R₃B and Et₂Be yields unsolvated BeR₂:



5.4. Formation of Bonds between Elements

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5.4.3. Formation of the Carbon—Group IIA-Element Bond

5.4.3.4. from Other Group-IIA Organometallics of the Same Metal

TABLE 1. REACTION CONDITIONS FOR 1:1 ADDITION OF ALKYLBERYLLIUM HYDRIDES TO ALKENE

Alkene	Reagent ^a	T (°C)	Half-life of alkene (h)	Ref.
1-Pentene	EtHBe·n OEt ₂	50	0.4	3
	EtHBe·n OEt ₂	33.5	4.85	3
	i-BuBeH	33.5	~0.2	5
	(i-BuHBe·OEt ₂) ₂	33.5	7–9	5
	(i-BuHBe·NMe ₃) ₂	33.5	20–25	5
	(H ₂ Be·NMe ₃) ₂	33.5	25	6
2-Pentene (95% cis)	EtHBe·n OEt ₂	50	≈ 90	3
2-Methylbut-2-ene	EtHBe·n OEt ₂	84	no reaction	3
	i-BuBeH	110	50	5

^a Benzene also present.

Internal alkenes react less readily with RBeH. The reactivity of 1-pentene to EtHBe·n OEt₂ is >200 times that of 2-pentene; the trialkylated ethene, 2-methylbut-2-ene, is inactive to addition of RBeH (R = Et, i-Bu) at 84°C and reacts only slowly with the more active, base-free i-BuBeH at 110°C (see Table 1)^{3,5}. Beryllium migrates to the end of the carbon chain as shown by the bromination of the products from 2-pentene and EtBeH: 82% 1-bromopentane, 12% 2-bromopentane and 6% 3-bromopentane³.

Thermal isomerization of t-Bu₂Be to i-Bu₂Be, which occurs slowly even at RT, proceeds by elimination and recombination by hydrometallation of 2-methylpropene with an intermediate beryllium hydride¹; a similar mechanism accounts for the racemization of (+)-Be[(R)—CH₂CH(Me)Et]₂.

Reactions of alkylberyllium hydrides with internal acetylenes, RC≡CR, are complex and involve both Be—H and Be—C addition to the acetylenic bond^{1,8}.

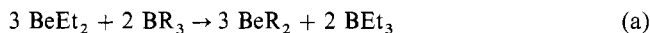
The hydrides MH₂ (M = Ca, Sr, Ba), suspended in organic solvents, react with alkenes (e.g., propene, 4 × 10⁻⁴ Nm⁻², 90 °C in toluene, M = Ca) in the presence of suitable catalysts (e.g., AlEt₃) to form alkylmetal compounds⁹.

(W. E. LINDSELL)

1. G. E. Coates, G. L. Morgan, *Adv. Organomet. Chem.*, **9**, 195 (1970). An authoritative review of organoberylliums.
2. G. E. Coates, D. L. Smith, R. C. Srivastava, *J. Chem. Soc., Dalton Trans.*, 618 (1973); and refs. therein.
3. N. A. Bell, G. E. Coates, *J. Chem. Soc., A*, 1069 (1966).
4. Montecatini, Br. Pat. 939,571 (1963); *Chem. Abstr.*, **60**, 3004 (1964); and earlier patents (see ref. 1).
5. G. E. Coates, P. D. Roberts, *J. Chem. Soc., A*, 1008 (1969).
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5.4.3.4.4. by Reaction with other Organometallics.

The exchange of organic groups between R₃B and Et₂Be yields unsolvated BeR₂:



Using ca. 3:2 $\text{BeEt}_2:\text{BR}_3$ in the absence of solvent, the following BeR_2 are formed in high yield and may be isolated by distillation in vacuo after removal of BeEt_3 by volatilization¹: $\text{R} = n\text{-Pr}$ (8 days, RT); $\text{R} = i\text{-Bu}$ (12 days, RT); $\text{R} = \text{Me}_3\text{CCH}_2$ (16 h, 70°C); $\text{R} = \text{Me}_3\text{SiCH}_2$ (8 days, RT). When $\text{R} = \text{Ph}$ exchange (a) may be achieved by mixing the reagents at RT for 36 h, evaporating the BeEt_3 produced at this stage (78 %), adding benzene and refluxing for a further 10 h to give BePh_2 (88 %), which separates as a solid on cooling²; $(p\text{-ClC}_6\text{H}_4)_2\text{Be}$ is formed, under identical conditions BeR_2 ($\text{R} = o\text{-}$ and $m\text{-tolyl}$, 2,5- $\text{C}_6\text{H}_3\text{Me}_2$) by mixing reagents at 25°C for 72 h, evaporating BeEt_3 and then heating in toluene at 90°C for 10 h, and $\text{Be}(1\text{-naphthyl})_2$ by heating the reagents in toluene at 100°C for 48 h².

Note that BeR_2 cannot be prepared by reaction (a) when $\text{R} = \text{mesityl}$, benzyl, $i\text{-propyl}$, cyclopentyl, cyclohexyl or pentafluorophenyl.² It is not possible to interchange BeMe_2 for BeEt_2 as a reagent in Eq. (a); thus no exchange occurs at 60°–70°C between BeMe_2 and BR_3 when $\text{R} = \text{Me}_3\text{CCH}_2$ (150 h) or $\text{R} = \text{Et}$ (72 h)¹, and this may reflect the higher energy required to depolymerize base-free Me_2Be . Also, reaction of BeEt_2 with $s\text{-Bu}_3\text{B}$ at RT forms a white involatile solid of composition Be_2HEt_3 originating from elimination of butene from an initially exchanged $s\text{-Bu}$ group¹.

Exchange (a) occurs rapidly when $\text{R} = \text{allyl}$ at 0°–60°C (or less) in the absence of solvent or in an aliphatic hydrocarbon, but the product, of composition $\text{C}_6\text{H}_{10}\text{Be}$, is not simply $\text{Be}(\text{allyl})_2$ because hydrolysis yields only 2–5 % propene³; $\text{C}_6\text{-}$, $\text{C}_9\text{-}$, $\text{C}_{12}\text{-}$, etc., hydrocarbons are formed instead, and these arise from oligomers produced by addition of monomeric $\text{Be}(\text{allyl})_2$ to the $\text{C}=\text{C}$ bond of another molecule (see §5.4.3.4.1). If reaction (a) is carried out in tetrahydrofuran (THF), the exchange is slower, but oligomerization takes place less readily and a species $(\text{C}_3\text{H}_5)_2\text{Be} \cdot 2 \text{ THF}$ is isolable that gives 49 % propene on hydrolysis³.

Exchange occurs in xylene at 90°C (15 h) to give BePh_2 in 78 % yield²:



The $\text{M}[\text{ZnEt}_4]$ ate complexes ($\text{M} = \text{Sr}$, Ba) undergo partial exchange with SnPh_4 and after 24 h at RT in ether, carbonation of the product affords PhCOOH [10.7 %, $\text{M} = \text{Sr}$; 32 %, $\text{M} = \text{Ba}$ (based on MEt_2 content of ate complex)]⁴. No analogous exchange is observed with MPh_4 ($\text{M} = \text{Si}$, Ge or Pb).

Redistribution may occur between two R_2Be compounds to form a mixed organo-metallic:

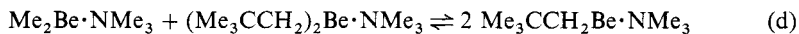


By dissolving 1:1 $\text{Be}(\text{Bu-t})_2:\text{BeR}_2$ in benzene and stirring at RT for ≤ 12 h (RBeBu-t_n , ($\text{R} = \text{Me}$, $n = 3$; $\text{R} = o\text{-tolyl}$, 2,5- $\text{C}_6\text{H}_3\text{Me}_2$, $n = 2$; $\text{R} = \text{cyclopentadienyl}$, $n = 1$) are isolable in quantitative yields on removal of solvent⁵; similarly monomeric complexes $\text{R}(\text{t-Bu})\text{Be} \cdot \text{TMED}$ ($\text{R} = o\text{-tolyl}$, $p\text{-tolyl}$, C_6F_5) are obtained on addition of tetramethylethylenediamine (TMED) to benzene solutions and $(\text{EtBeBu-t})_2$ is produced in the absence of solvent⁵. These $t\text{-Bu}$ derivatives yield RBUH by thermal elimination of 2-methylpropene.

Cyclopentadienyl derivatives $\text{h}^5\text{-C}_5\text{H}_5\text{BeR}$ are obtained by reaction (c); when $\text{R} = \text{C}_6\text{F}_5$ the product is produced in benzene after 30 h at RT⁵; when $\text{R} = \text{Me}$ reaction occurs in benzene, but the product does not separate from solvent and reaction in the absence of solvent at 50°C using xs BeMe_2 allows easier isolation of liq $\text{h}^5\text{-C}_5\text{H}_5\text{BeMe}$ by

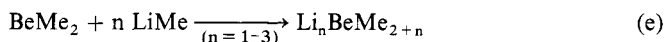
distillation from less volatile BeMe_2 ⁶. Redistribution in a solvent-free system is also recommended for the preparation of $\text{h}^5\text{-C}_5\text{H}_5\text{BeR}$ ($\text{R} = \text{Et, n-Bu, t-Bu}$)⁷.

The crystalline alkynyl-bridged dimers, $[(\text{MeBe}\cdot\text{NMe}_3)_2(\mu\text{-C}\equiv\text{CR})]_2$ ($\text{R} = \text{Me, t-Bu}$) are formed from 1:2 mixtures of $[(\text{RC}\equiv\text{C})_2\text{Be}\cdot\text{NMe}_3]_2$ and $\text{Me}_2\text{Be}\cdot\text{NMe}_3$ in benzene or toluene at RT⁸. The equilibrium between the Me_3N adducts:



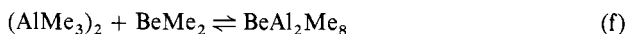
has $K = 170$ at -40°C , and the $\text{Me}_3\text{CCH}_2\text{Be}\cdot\text{TMED}$ complex is obtained by adding TMED to $(\text{Me}_3\text{CCH}_2)_2\text{Be}\cdot\text{OEt}_2$ and BeMe_2 in benzene⁹.

Combination of 1:1 $\text{BePh}_2\text{:LiPh}$ in Et_2O forms the ate complex LiBePh_3 , which, after removal of solvent, may be recrystallized from xylene¹⁰; the complex LiBe(o-tolyl)_3 is synthesized similarly², and $\text{Na}[\text{BePh}_2(\text{CPh}_3)]$ is obtained¹⁰ from BePh_2 and NaCPh_3 . The tetramethylberyllate, Li_2BeMe_4 , containing a distorted tetrahedral BeMe_4 unit in the solid, is prepared¹¹ by mixing BeMe_2 and LiMe (1:2) in Et_2O . After removal of most of the solvent, addition of hexane and slow evaporation at low T yields microcrystalline Li_2BeMe_4 . The three complexes LiBeMe_3 , Li_2BeMe_4 and Li_3BeMe_5 are present in Et_2O containing appropriate stoichiometric mixtures¹² of BeMe_2 and LiMe_2 :

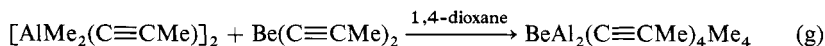


Variable-T spectroscopy shows that although Eq. (e) is the principal reaction, each complex exists in equilibrium with others in solution. Mixing 2:1 $\text{BeMe}_2\text{:LiMe}$ in Et_2O gives LiBe_2Me_5 , but it is not clear whether this is a discrete complex or a mixture of LiBeMe_3 and BeMe_2 in equilibrium¹². Mixing $\text{LiC}\equiv\text{CPh}$ and $\text{Be}(\text{C}\equiv\text{CPh})_2 \cdot 2\text{THF}$ in THF at RT affords insoluble $\text{Li}_2\text{Be}(\text{C}\equiv\text{CPh})_4$ ¹³.

The interactions of $[\text{AlMe}_3]_2$ and BeMe_2 , in hydrocarbons is reversible, but ^1H NMR identifies the 2:1 ate complex at -90°C ¹⁴:



By reaction initially for 4 h at 80°C and subsequently 6 h at RT the $\text{Be}(\mu\text{-C}\equiv\text{CMe})_4(\text{AlMe}_2)_2$ complex is obtained as a pale yellow solid (84%)¹⁵:



Reactions of RCaI ($\text{R} = \text{alkyl, aryl}$) with LiR' give uncharacterized ate complexes, which are formulated $\text{Li}[\text{CaRR'I}]$ ⁴.

(W. E. LINDSELL)

1. G. E. Coates, B. R. Francis, *J. Chem. Soc., A*, 1308 (1971).
2. G. E. Coates, R. C. Srivastava, *J. Chem. Soc., Dalton Trans.*, 1541 (1972).
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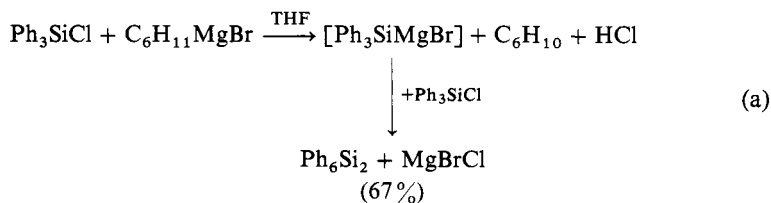
5.4.4. Formation of the Si—Group IIA-Element Bond

5.4.4.1. from the Elements

This topic is dealt with in §5.10.3.

5.4.4.2. from Organohalosilanes with a Group-IIA Branched Metal-Organic Reagent.

When Ph_3SiCl is refluxed for ≥ 18 h with $\text{C}_6\text{H}_{11}\text{MgBr}$ in tetrahydrofuran (THF), Ph_6Si_2 is produced. The nature of the reaction products indicates, however, that an organosilylmagnesium intermediate is formed:



This intermediate couples with an additional molecule of Ph_3SiCl . When Me_3SiCl is taken instead of Ph_3SiCl , no disilane is formed. When a mixture of Me_3SiCl and Ph_3SiCl is treated with $\text{C}_6\text{H}_{11}\text{MgBr}$, the unsymmetrical disilane, $\text{Me}_3\text{SiSiPh}_3$ is produced in 14 % yield¹.

(L. RÖSCH)

1. T. G. Selin, R. West, *Tetrahedron*, **5**, 97 (1959).

5.4.4.3. from Organohalosilanes with Mg Metal

Organosilyl magnesiums are synthesized via halo- or organohalosilanes with Mg metal. Disilanes are produced, suggesting that an intermediate silylmagnesium may be formed. The best results are obtained when chloroarylsilanes are reacted in tetrahydrofuran (THF). Chloroalkylsilanes, such as Me_3SiCl , react only under specific conditions. These reactions are only useful for disilanes (see also §5.2.3.4); Si—Mg bonded compounds are formed only as reactive intermediates. Older work is reviewed in ref. 1. newer work in refs. 2–6.

(L. RÖSCH)

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5.4. Formation of Bonds between Elements

5.4.4. Formation of the Si—Group IIA-Element Bond

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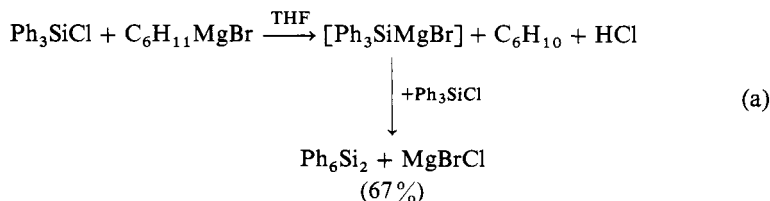
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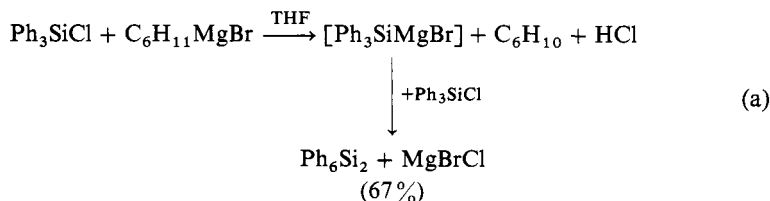
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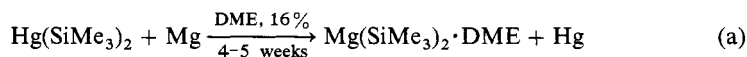
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(L. RÖSCH)

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2. C. L. Smith, R. Gooden, *J. Organomet. Chem.*, **81**, 45 (1974).
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5.4.4.4. from Bis(silyl)mercurials with Mg Metal

The slow reaction of $\text{Hg}(\text{SiMe}_3)_2$ with Mg metal produces a silylmagnesium in 1,2-dimethoxyethane (DME) in low yield:



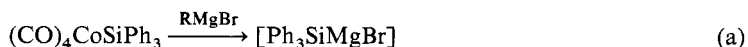
The desired compound is isolated by crystallization¹ or by sublimation at 40 °C in high vacuum². In tetrahydrofuran (THF), $\text{Mg}(\text{SiMe}_3)_2 \cdot 2 \text{ THF}$ is generated¹. In vacuum one THF is lost and $\text{Mg}(\text{SiMe}_3)_2 \cdot \text{THF}$ is isolated. When 1,3-bis(dimethylamino)propane (TMDAP)/ Et_2O is used, $\text{Mg}(\text{SiMe}_3)_2 \cdot \text{TMDAP}$ forms⁶ while the DME adduct can be prepared in high yield from Mg powder and $\text{Hg}(\text{SiMe}_3)_2$ in a supersonic DME bath³; likewise, $\text{Mg}(\text{SiEt}_3)_2 \cdot \text{DME}$ is obtained⁴. Reaction of $\text{Hg}(\text{SiMe}_2\text{Ph})_2$ with Mg metal cleaves a methyl group from DME, yielding a complex cation with Mg^{2+} ; $\text{Mg}(\text{SiMe}_2\text{Ph})_2$ cannot be obtained⁵. When $\text{Mg}(\text{SiMe}_3)_2 \cdot \text{DME}$ is treated with tetramethylethylenediamine (TMED), the TMED adduct is isolated⁷.

(L. RÖSCH)

1. A. R. Clagett, W. H. Ilsley, T. J. Anderson, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **99**, 1797 (1977).
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5.4.4.5. from an Organosilyl-Transition-Metal Complex with an Organomagnesium-Halide Reagent.

Silyl-Mg bonds are formed from an organosilyl-transition-metal complex with an organomagnesium halide reagent. Treatment of $(\text{CO})_4\text{CoSiPh}_3$ with a tenfold xs of the reagent leads to Ph_3SiMgBr :



where R = Me, Et, allyl. The silylmagnesium product cannot be isolated; a Si—Mg bond is established by further reaction¹.

5.4. Formation of Bonds between Elements

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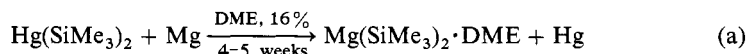
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3. P. Gervais, E. Frainnet, G. Lain, F. Moulines, *Bull. Soc. Chim. Fr.*, 1548 (1974).
4. L. Rösch, W. Erb, H. Müller, *Z. Naturforsch., Teil B*, **31**, 281 (1976).
5. R. Calas, J. Dunogues, *J. Organomet. Chem. Libr.*, **2**, 277 (1976).
6. V. D. Sheludyakov, V. I. Zhun', G. N. Turkel'taub, M. V. Polyakova, M. G. Kuznetsova, A. A. Bernadskii, V. F. Mironov, *J. Gen. Chem. USSR (Engl. Transl.)*, **45**, 912 (1979).

5.4.4.4. from Bis(silyl)mercurials with Mg Metal

The slow reaction of $\text{Hg}(\text{SiMe}_3)_2$ with Mg metal produces a silylmagnesium in 1,2-dimethoxyethane (DME) in low yield:



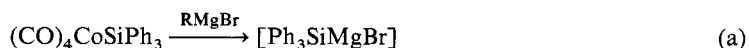
The desired compound is isolated by crystallization¹ or by sublimation at 40 °C in high vacuum². In tetrahydrofuran (THF), $\text{Mg}(\text{SiMe}_3)_2 \cdot 2 \text{ THF}$ is generated¹. In vacuum one THF is lost and $\text{Mg}(\text{SiMe}_3)_2 \cdot \text{THF}$ is isolated. When 1,3-bis(dimethylamino)propane (TMDAP)/ Et_2O is used, $\text{Mg}(\text{SiMe}_3)_2 \cdot \text{TMDAP}$ forms⁶ while the DME adduct can be prepared in high yield from Mg powder and $\text{Hg}(\text{SiMe}_3)_2$ in a supersonic DME bath³; likewise, $\text{Mg}(\text{SiEt}_3)_2 \cdot \text{DME}$ is obtained⁴. Reaction of $\text{Hg}(\text{SiMe}_2\text{Ph})_2$ with Mg metal cleaves a methyl group from DME, yielding a complex cation with Mg^{2+} ; $\text{Mg}(\text{SiMe}_2\text{Ph})_2$ cannot be obtained⁵. When $\text{Mg}(\text{SiMe}_3)_2 \cdot \text{DME}$ is treated with tetramethylethylenediamine (TMED), the TMED adduct is isolated⁷.

(L. RÖSCH)

1. A. R. Clagett, W. H. Ilsley, T. J. Anderson, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **99**, 1797 (1977).
2. L. Rösch, *Angew. Chem. Int. Ed. Engl.*, **16**, 247 (1977).
3. L. Rösch, U. Starke, *Z. Naturforsch., Teil B*, **38**, 1292 (1983).
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5. E. A. Sadurski, W. H. Ilsley, R. D. Thomas, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **100**, 7761 (1978).
6. L. Rösch, J. Pickardt, S. Imme, U. Börner, *Z. Naturforsch., Teil B*, in press.
7. D. N. Goebel, Jr., I. L. Hencher, J. P. Oliver, *Organometallics*, **2**, 746 (1983).

5.4.4.5. from an Organosilyl-Transition-Metal Complex with an Organomagnesium-Halide Reagent.

Silyl-Mg bonds are formed from an organosilyl-transition-metal complex with an organomagnesium halide reagent. Treatment of $(\text{CO})_4\text{CoSiPh}_3$ with a tenfold xs of the reagent leads to Ph_3SiMgBr :



where R = Me, Et, allyl. The silylmagnesium product cannot be isolated; a Si—Mg bond is established by further reaction¹.

5.4. Formation of Bonds between Elements

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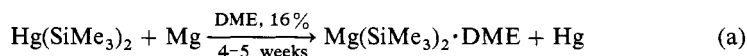
5.4.4. Formation of the Si-Group IIA-Element Bond

5.4.4.5. from an Organosilyl-Transition-Metal Complex

1. D. D. Davies, C. E. Gray, *Organomet. Chem. Rev. A*, **6**, 283 (1970).
2. C. L. Smith, R. Gooden, *J. Organomet. Chem.*, **81**, 45 (1974).
3. P. Gervail, E. Frainnet, G. Lain, F. Moulines, *Bull. Soc. Chim. Fr.*, 1548 (1974).
4. L. Rösch, W. Erb, H. Müller, *Z. Naturforsch., Teil B*, **31**, 281 (1976).
5. R. Calas, J. Dunogues, *J. Organomet. Chem. Libr.*, **2**, 277 (1976).
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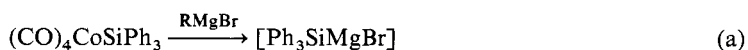
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3. L. Rösch, U. Starke, *Z. Naturforsch., Teil B*, **38**, 1292 (1983).
4. U. Starke, Ph.D. Thesis, Tech. Univ. Berlin, 1975.
5. E. A. Sadurski, W. H. Ilsley, R. D. Thomas, M. D. Glick, J. P. Oliver, *J. Am. Chem. Soc.*, **100**, 7761 (1978).
6. L. Rösch, J. Pickardt, S. Imme, U. Börner, *Z. Naturforsch., Teil B*, in press.
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where R = Me, Et, allyl. The silylmagnesium product cannot be isolated; a Si—Mg bond is established by further reaction¹.

Treatment of optically active $(\text{CO})_4\text{CoSiMePh}(\alpha\text{-Np})$ (Np = naphthyl) with MeMgBr yields a silyl reagent, $\alpha\text{-NpPhMeSiMgBr}$, of low optical activity¹:

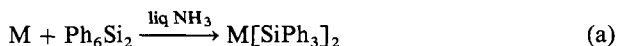


(L. RÖSCH)

1. E. Colomer, R. Corriu, *J. Chem. Soc. Chem. Commun.*, 176 (1976).

5.4.4.6. from Hexaphenyldisilane with a Group-IIA Metal

Solutions of Ca, Sr or Ba in liq NH_3 react with Ph_6Si_2 to form $\text{Ca}[\text{SiPh}_3]_2$, $\text{Sr}[\text{SiPh}_3]_2$ and $\text{Ba}[\text{SiPh}_3]_2$:



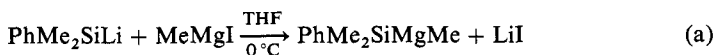
where when $\text{M} = \text{Ca}$ or Sr only trace, yields are obtained, and, when $\text{M} = \text{Ba}$, a good yield is obtained. No reaction occurs in tetrahydrofuran (THF)¹.

(L. RÖSCH)

1. E. Wiberg, O. Stecher, H.-J. Andrascheck, L. Kreuzbichler, E. Staude, *Angew. Chem., Int. Ed. Eng.*, 2, 507 (1963).

5.4.4.7. from Organosilyllithium with an Organomagnesium-Halide Reagent

From PhMe_2SiLi with MeMgI in THF, $\text{PhMe}_2\text{SiMgMe}$ forms:



The silylmagnesium product was not isolated; the Si—Mg bond is established by further reaction¹⁻³.

(L. RÖSCH)

1. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, H. Nozaki, *J. Am. Chem. Soc.*, 105, 4491 (1983).
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5.4.5. The Formation of the Germanium—Group-IIA Element Bond

5.4.5.1. from the Elements

This topic is dealt with in §5.10.4.1.

(L. RÖSCH)

- 324 5.4. Formation of Bonds between Elements
 5.4.5. The Formation of the Germanium—Group-IIA Element Bond
 5.4.5.1. from the Elements

Treatment of optically active $(\text{CO})_4\text{CoSiMePh}(\alpha\text{-Np})$ (Np = naphthyl) with MeMgBr yields a silyl reagent, $\alpha\text{-NpPhMeSiMgBr}$, of low optical activity¹:

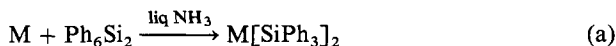


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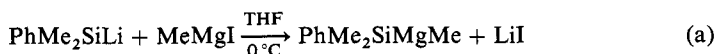
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(L. RÖSCH)

1. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, H. Nozaki, *J. Am. Chem. Soc.*, 105, 4491 (1983).
2. Y. Okuda, M. Sato, K. Oshima, H. Nozaki, *Tetrahedron Lett.*, 24, 2015 (1983).
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- 324 5.4. Formation of Bonds between Elements
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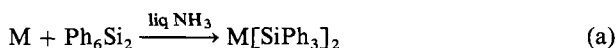


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5.4.4.6. from Hexaphenyldisilane with a Group-IIA Metal

Solutions of Ca, Sr or Ba in liq NH_3 react with Ph_6Si_2 to form $\text{Ca}[\text{SiPh}_3]_2$, $\text{Sr}[\text{SiPh}_3]_2$ and $\text{Ba}[\text{SiPh}_3]_2$:



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5.4.5. The Formation of the Germanium—Group-IIA Element Bond

5.4.5.1. from the Elements

This topic is dealt with in §5.10.4.1.

(L. RÖSCH)

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5.4. Formation of Bonds between Elements

5.4.5. The Formation of the Germanium—Group-IIA Element Bond

5.4.5.1. from the Elements

Treatment of optically active $(\text{CO})_4\text{CoSiMePh}(\alpha\text{-Np})$ (Np = naphthyl) with MeMgBr yields a silyl reagent, $\alpha\text{-NpPhMeSiMgBr}$, of low optical activity¹:

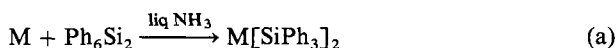


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where when $\text{M} = \text{Ca}$ or Sr only trace, yields are obtained, and, when $\text{M} = \text{Ba}$, a good yield is obtained. No reaction occurs in tetrahydrofuran (THF)¹.

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5.4.4.7. from Organosilyllithium with an Organomagnesium-Halide Reagent

From PhMe_2SiLi with MeMgI in THF, $\text{PhMe}_2\text{SiMgMe}$ forms:



The silylmagnesium product was not isolated; the Si—Mg bond is established by further reaction¹⁻³.

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5.4.5. The Formation of the Germanium—Group-IIA Element Bond

5.4.5.1. from the Elements

This topic is dealt with in §5.10.4.1.

(L. RÖSCH)

5.4.5.2. from Ge Halides or Organogermanium Halides with a Group-IIA Metal or Organomagnesium-Halide Reagent

Treatment of GeCl_4 with certain organomagnesium halide reagents gives intermediates with Ge—Mg bonds, e.g., Ph_3GeMgBr , which cannot be isolated. The Ge—Mg bond is established by the formation of digermanes or by the generation of R_3GeH after hydrolysis¹. These reactions have only limited importance for the synthesis of digermanes or germanes, and the species with a Ge—Mg bond is only an intermediate.

A reagent exhibiting all the properties of an organomagnesium-halide reagent forms directly from Mg and Ph_3GeCl in hexamethylphosphoramide (HMPA).



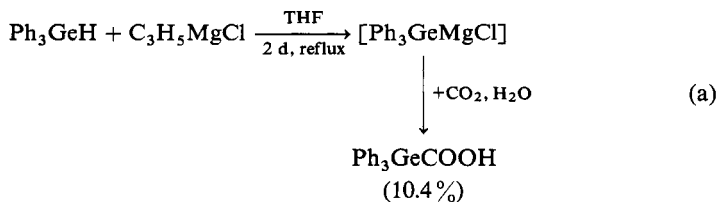
Deuteriolysis with D_2O gives Ph_3GeD in 55% yield².

(L. RÖSCH)

1. M. Lesbre, P. Mazerolles, J. Satgé *The Organic Compounds of Germanium*, J. Wiley, New York, 1971.
2. J. C. Mendelsohn, Thesis, Univ. Bordeaux, 1966 (cited in ref. 1).

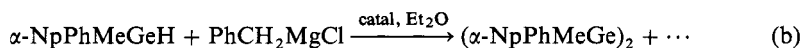
5.4.5.3. from Organogermanium Hydrides with an Organomagnesium Halide-Reagent

A germylmagnesium can be generated from an organogermanium hydride with an organomagnesium-halide reagent. The reaction of Ph_3GeH with allylmagnesium chloride in refluxing tetrahydrofuran (THF) gives Ph_3GeMgCl with other products. The germylmagnesium chloride reagent is confirmed by carbonation, which affords Ph_3GeCOOH is a 10% yield.



The germylmagnesium-chloride reagent attacks the solvent to form¹ $\text{Ph}_3\text{Ge}(\text{CH}_2)_4\text{OH}$. Generation of Ph_3GeMgCl is also postulated when Ph_3GeH is treated with other organomagnesium-halide reagents¹. When Ph_3GeD is reacted with PhCH_2MgCl in Et_2O at 21°C for 6 days, Ph_3GeH is obtained after hydrolysis in 4% yield².

An optically active digermane is obtained from $\alpha\text{-NpPhMeGeH}$ with PhCH_2HgCl , activated by a Ni catalyst:



When catal = NiCl_2 , the yield is 16%; when catal = $(\text{Ph}_3\text{P})_2\text{NiCl}_2$, yield is 22%. The formation of the digermane indicates, that $\alpha\text{-NpPhMeGeMgCl}$ is an intermediate².

(L. RÖSCH)

5.4. Formation of Bonds between Elements

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5.4.5. The Formation of the Germanium–Group-IIA Element Bond

5.4.5.3. from Organogermanium Hydrides

5.4.5.2. from Ge Halides or Organogermanium Halides with a Group-IIA Metal or Organomagnesium-Halide Reagent

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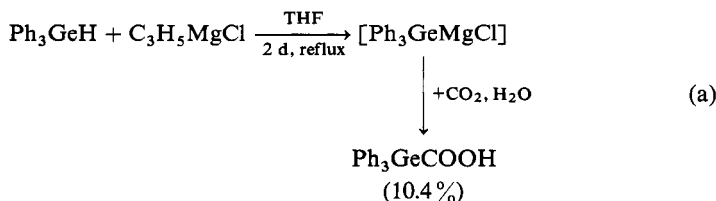
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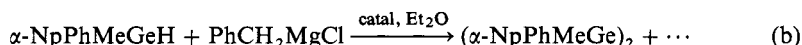
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1. H. Gilman, E. A. Zuech, *J. Org. Chem.*, **26**, 3035 (1961).

2. F. Carre, R. Corriu, *J. Organomet. Chem.*, **73**, C49 (1974).

5.4.5.4. from a Triphenylgermyl–Transition-Metal Complex with an Organomagnesium-Halide Reagent

Treatment of $(\text{OC})_4\text{CoGePh}_3$ with MeMgBr leads to substitution on Ge, whereas $\text{C}_3\text{H}_5\text{MgBr}$ leads to a germylmagnesium-halide reagent:



The formation of a Ge—Mg bond in this reaction is established by hydrolysis with H_2O or D_2O , yielding Ph_3GeH or the deuteriated germane¹.

(L. RÖSCH)

1. E. Colomer, R. Corriu, *J. Chem. Soc., Chem. Commun.*, 176 (1976).

5.4.5.5. from Bis(germyl)mercurials with Mg Metal

The reaction of $\text{Hg}(\text{GeMe}_3)_2$ with Mg metal in 1,2-dimethoxyethane (DME) delivers $\text{Mg}(\text{GeMe}_3)_2 \cdot 2 \text{ DME}$, the only organogermanium–Mg obtained pure:



The compound is isolated by crystallization from the solvent and purified by recrystallization from Et_2O ^{1,2}.

(L. RÖSCH)

1. L. Rösch, *Angew. Chem., Int. Ed. Engl.*, **20**, 872 (1981).

2. L. Rösch, C. Krüger, A.-P. Chiang, *Z. Naturforsch., Teil B*, **39**, 855 (1984).

5.4.5.6. from Hexaaryldigermanes with Mg, Ca, Sr, Ba

Group-IIA metals insert into the Ge—Ge bond (cf. §5.2.11.6):



where M = Mg, Ca, Sr, Ba. Reaction of Ph_6Ge_2 with Mg metal in hexamethylphosphoramide (HMPA) results in a reagent¹ exhibiting the properties of an organomagnesium-halide reagent, $(\text{Ph}_3\text{Ge})_2\text{Mg}$. No product is isolated. Calcium metal behaves similarly².

Hexaphenyldigermane reacts with 1:1 Sr or Ba metal in liq NH_3 at -40°C and yields solutions of $(\text{Ph}_3\text{Ge})_2\text{Sr}$ and $(\text{Ph}_3\text{Ge})_2\text{Ba}$. The NH_3 is removed and the residue extracted with tetrahydrofuran (THF) at -35°C . The THF is removed in vacuo (2 days at 40°C). The yellow solid residues are sensitive to air and light and contain 1 mol THF³.

(M. DRÄGER)

1. J. C. Mendelsohn, Thesis, Univ. Bordeaux, 1966; cited in M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley, London, 1971, p. 657.

2. K. Mochida, M. Manishi, *Chem. Lett.*, 1077 (1984).

3. E. Amberger, W. Stoeger, R. Hönigschmid-Grossich, *Angew. Chem., Int. Ed. Engl.*, **5**, 522 (1966).

5.4. Formation of Bonds between Elements

5.4.5. The Formation of the Germanium-Group-IIA Element Bond

5.4.5.6. from Hexaaryldigermanes with Mg, Ca, Sr, Ba

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Group-IIA metals insert into the Ge—Ge bond (cf. §5.2.11.6):



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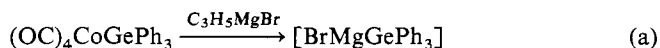
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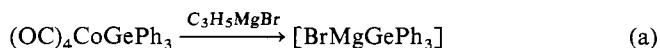
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5.4. Formation of Bonds between Elements

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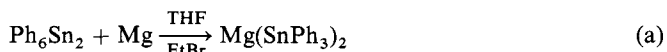
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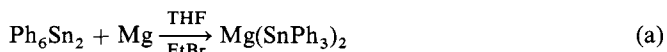
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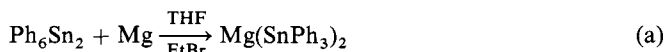
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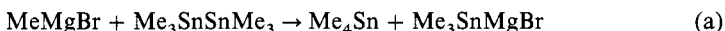
328 5.4. Formation of Bonds between Elements

5.4.6. Formation of the Tin-Group-IIA Element Bond

5.4.6.6. from Sn(II) Compounds with Organomagnesium-Halide Reagents

5.4.6.4. from Hexaorganodistannanes with Organomagnesium-Halide Reagents

A tin-organomagnesium halide compound forms as an intermediate when Me_6Sn_2 is reacted with other R_6Sn_2 compounds ($\text{R} = \text{Et}, n\text{-Pr}, n\text{-Bu}, i\text{-Bu}$) in tetrahydrofuran (THF) or MeCN in presence of an MeMgBr catalysis:



The final products are asymmetrical hexaalkylditins. The Sn-Mg compound is not isolated¹.

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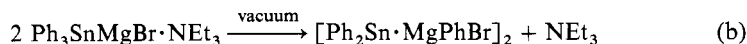
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The most common way to get organotin-Mg compounds is from organotin hydrides with an organomagnesium-halide reagent. The 1:1 reaction of Ph_3SnH with $\text{EtBrMg} \cdot \text{NEt}_3$ in Et_2O at -15 to 0°C results in selective hydrostannolysis of the Mg-C bond as evidenced by the quantitative formation of ethane:



The compound can be isolated as an Et_2O insoluble oil. The composition is confirmed by further reactions¹. In vacuum, NEt_3 is split off, and phenyl group transfer from Sn to Mg occurs:



The phenyl shift can be reversed with complexing ligands such as Et_2O and tetramethylethylenediamine (TMED)¹.

The organotin-Mg compound Bu_3SnMgCl finds application in synthetic chemistry²⁻⁶. It is obtained from Bu_3SnH with organomagnesium-halide reagents ($\text{R} = i\text{-Pr}, s\text{-Bu}, t\text{-Bu}, c\text{-C}_6\text{H}_{11}$)^{2,3}:



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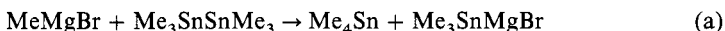
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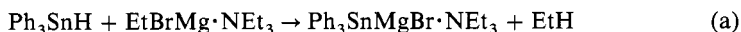
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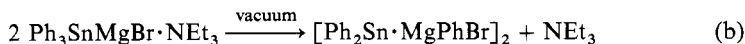
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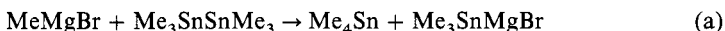
328 5.4. Formation of Bonds between Elements

5.4.6. Formation of the Tin-Group-IIA Element Bond

5.4.6.6. from Sn(II) Compounds with Organomagnesium-Halide Reagents

5.4.6.4. from Hexaorganodistannanes with Organomagnesium-Halide Reagents

A tin-organomagnesium halide compound forms as an intermediate when Me_6Sn_2 is reacted with other R_6Sn_2 compounds ($\text{R} = \text{Et}, n\text{-Pr}, n\text{-Bu}, i\text{-Bu}$) in tetrahydrofuran (THF) or MeCN in presence of an MeMgBr catalysis:



The final products are asymmetrical hexaalkylditins. The Sn-Mg compound is not isolated¹.

(L. RÖSCH)

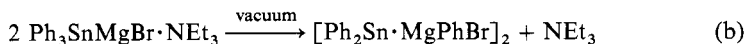
1. E. Bulten, H. A. Buding, *J. Organomet. Chem.*, **78**, 385 (1975).

5.4.6.5. from Organotin Hydrides with Organomagnesium-Halide Reagents

The most common way to get organotin-Mg compounds is from organotin hydrides with an organomagnesium-halide reagent. The 1:1 reaction of Ph_3SnH with $\text{EtBrMg} \cdot \text{NEt}_3$ in Et_2O at -15 to 0°C results in selective hydrostannolysis of the Mg-C bond as evidenced by the quantitative formation of ethane:



The compound can be isolated as an Et_2O insoluble oil. The composition is confirmed by further reactions¹. In vacuum, NEt_3 is split off, and phenyl group transfer from Sn to Mg occurs:



The phenyl shift can be reversed with complexing ligands such as Et_2O and tetramethylethylenediamine (TMED)¹.

The organotin-Mg compound Bu_3SnMgCl finds application in synthetic chemistry²⁻⁶. It is obtained from Bu_3SnH with organomagnesium-halide reagents ($\text{R} = i\text{-Pr}, s\text{-Bu}, t\text{-Bu}, c\text{-C}_6\text{H}_{11}$)^{2,3}:



The best yield is obtained when $i\text{-PrMgCl}$ is used².

(L. RÖSCH)

1. H. M. J. C. Creemers, J. G. Noltes, G. J. M. van der Kerk, *J. Organomet. Chem.*, **14**, 217 (1968).
2. J.-C. Lahournère, J. Valade, *J. Organomet. Chem.*, **22**, C3 (1970).
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4. J.-C. Lahournère, J. Valade, *J. Organomet. Chem.*, **33**, C4 (1971).
5. J.-P. Quintard, B. Elisondo, M. Pereyre, *J. Organomet. Chem.*, **212**, C31 (1981).
6. J.-C. Lahournère, J. Valade, *J. Organomet. Chem.*, **33**, C7 (1971).

5.4.6.6. from Sn(II) Compounds with Organomagnesium-Halide Reagents

The addition of $(h^5\text{-C}_5\text{H}_5)_2\text{Sn}$ or $(h^5\text{-MeC}_5\text{H}_4)_2\text{Sn}$ to PhMgBr in Et_2O results¹ in the immediate precipitation of yellow $\text{Ph}(\text{C}_5\text{H}_5)_2\text{SnMgBr}$ or $\text{Ph}(\text{MeC}_5\text{H}_4)_2\text{SnMgBr}$:



where $\text{R} = \text{H}, \text{CH}_3$.

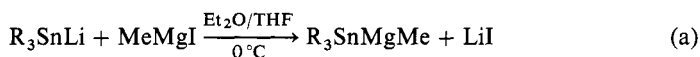
The reaction of Ph_2Sn with PhMgBr , in contrast to Eq. (a), leads to a compound that behaves like an adduct of Ph_2Sn with PhMgBr .

(L. RÖSCH)

1. P. G. Harrison, J. J. Zuckerman, J. G. Noltes, *J. Organomet. Chem.*, 31, C23 (1971).

5.4.6.7. from Stannyl-Alkali-Metal Reagents with Organomagnesium-Halide Reagents

A tin-organomagnesium compound is formed when R_3SnLi reacts with MeMgI^1 :



where $\text{R} = \text{Me}, \text{n-Bu}$. The compounds are not isolated, but the solutions taken for further reactions^{1,2}.

(L. RÖSCH)

1. J. Hibino, S. Matsubara, Y. Morizawa, K. Oshima, H. Nozaki, *Tetrahedron Lett.*, 25, 2151 (1984).
2. S. Matsubara, J. Hibino, Y. Morizawa, K. Oshima, H. Nozaki, *J. Organomet. Chem.*, 285, 163 (1985).

5.4.7. Formation of the Lead–Group-IIA Bond

5.4.7.1. Lead–Group-IIA Alloys and Intermetallic Compounds

Lead forms alloys and intermetallic compounds with Mg , Ca , Sr and Ba , but not with Be . No experiment to prepare Pb-Ra alloys is reported.

(F. HUBER, K. GRÄTZ)

5.4.7.1.1. from the Elements.

Lead and Be mix neither in the melt nor in the solid state¹.

Alloys of Pb and Mg , Ca , Sr or Ba can be prepared in all proportions. These are fused at ca. $700^\circ\text{--}800^\circ\text{C}$ in magnesite, corundum, graphite, etc., crucibles under cover or in an inert gas.

Lead– Mg alloys are prepared readily, because Mg metal is easily soluble in molten Pb metal, and any convenient method of preparation may be employed, e.g., the components may be fused under a cover of KCl or MgCl_2 , or in H_2 or inert gas at $700^\circ\text{--}800^\circ\text{C}$, and after mixing and cooling in the absence of air the product can be broken up^{2–4}. To prepare alloys with $> 50 \text{ wt } \%$ Mg , first Mg metal is melted, and Pb is added, whereas Mg is added to molten Pb to prepare alloys with $> 50 \text{ wt } \%$ Pb ^{3,4}.

Lead– Ca Pb-Sr and Pb-Ba alloys are obtained analogously.

Intermetallics can be prepared from the stoichiometric components either by fusing or by dissolving one component in the melt of the other in an inert atmosphere.

5.4. Formation of Bonds between Elements

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5.4.7. Formation of Lead-Group-IIA Bond

5.4.7.1. Lead-Group-IIA Alloys and Intermetallic Compounds

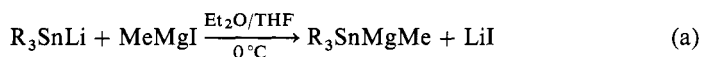
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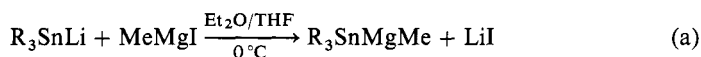
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Lead- Ca Pb-Sr and Pb-Ba alloys are obtained analogously.

Intermetallics can be prepared from the stoichiometric components either by fusing or by dissolving one component in the melt of the other in an inert atmosphere.

Formation of Mg_2Pb is accomplished by melting stoichiometric amounts of Mg and Pb (19.06 wt% and 80.94 wt%, respectively) with stirring and excluding air^{3,5} (e.g., in H_2 ⁶) or in vacuo not $> 600^\circ\text{C}$ ^{6,7,8}; a pure product, which can be used as semiconductor is prepared by allowing Mg vapor to diffuse into molten Pb metal⁹.

Four intermetallic compounds, Ca_2Pb , CaPb_3 , Ca_5Pb_3 and CaPb , are prepared by fusing stoichiometric Ca and Pb in Fe or Ta crucibles, which are sealed under Ar^{10,11} or which are heated under Ar¹² or in a glass tube in a stream of H_2 ¹³.

In the Pb-Sr system seven intermetallic compounds¹⁴, and in the Pb-Ba system five intermetallic compounds^{13,14} are identified: Sr_2Pb , SrPb_3 , Sr_5Pb_3 , Sr_5Pb_4 , SrPb , Sr_2Pb_3 , Sr_3Pb_5 and BaPb_3 , BaPb , Ba_5Pb_3 , Ba_3Pb_5 , Ba_2Pb , respectively. They are prepared from the elements in sealed Fe crucibles as are the Pb-Ca compounds^{14,15,17-19}.

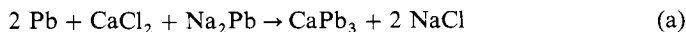
Ternary alloys and intermetallic compounds are obtained similarly; e.g., MgNaPb ¹⁷ and $\text{Mg}_4\text{Na}_4\text{Pb}_3$ ¹⁸ are prepared by fusing mixtures of Mg, Pb and NaPb or Na_4Pb alloy in N_2 or He in sealed Fe bombs at 650° and 725°C , respectively, with intermittent shaking. The alloy is allowed to cool slowly.

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1. M. Fröhlich, Ph.D. Diss, Univ. Mainz, 1958, p. 85; quoted in *Gmelins Handbuch der Anorganischen Chemie*, 8th ed., Blei 47, C3, Verlag Chemie, Weinheim, 1970, p. 1159.
2. J. Parkinson, *J. Chem. Soc.*, 20, 121 (1867).
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6. W. Klemm, H. Westlinning, *Z. Anorg. Allg. Chem.*, 245, 365 (1941).
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12. M. Nouri, A. Morrison, M. C. Baron, C. Petot, *Thermochim. Acta*, 90, 207 (1985).
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19. F. Merlo, *Rev. Chem. Minér.*, 21, 78 (1984).
20. G. Calingaert, H. Shapiro, I. T. Krohn, *J. Am. Chem. Soc.*, 70, 270 (1948).
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5.4.7.1.2. by Reduction.

Lead-Ca alloys and intermetallics are prepared by reduction of Ca compounds with Pb, Al, C, Pb-Al or Pb-Na alloys, e.g., CaPb_3 is produced¹ by the chloride process:



The product contains Na when Pb-Na alloy is used as reducing agent.

Alloys of Pb with Ca, Sr, Ba can also be prepared from molten alkaline-earth halides by reduction with Pb-Na alloys; however, electrolytic preparation is more efficient².

5.4. Formation of Bonds between Elements

5.4.7. Formation of the Lead-Group-IIA Bond

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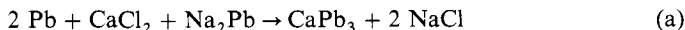
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The product contains Na when Pb-Na alloy is used as reducing agent.

Alloys of Pb with Ca , Sr , Ba can also be prepared from molten alkaline-earth halides by reduction with Pb-Na alloys; however, electrolytic preparation is more efficient².

A common procedure is the carbide process or carbide–thermal method in which CaC_2 either is reacted with molten Pb metal:



or is reduced, e.g., by Al in the presence of molten Pb metal in an inert or reducing atmosphere at ca. 1000°C in the presence of a flux^{2–5}. The Ca metal formed during these reactions and Pb metal yield CaPb_3 and Ca–Pb alloy, the composition depending on the stoichiometry.

As the source of Ca instead of CaCl_2 or CaC_2 CaO can also be used. It is reduced by Al metal in the presence of CaCl_2 and NaCl (as flux) in molten Pb metal⁶.

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5.4.7.1.3. by Electrolysis.

The preparation of binary alloys of Pb and Mg^1 , Ca^{2-4} , Sr^4 or Ba^4 also can be performed by electrolysis of salt melts at a liq Pb metal cathode using fluorides as flux at ca. $700^\circ\text{--}800^\circ\text{C}$ and graphite anodes. In all cases air must be excluded.

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1. E. A. Ashcroft, *Trans. Faraday Soc.*, **14**, 273 (1919).
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3. W. Siecke, *Ger. Pat.* 584,399 (1933); *Chem. Abstr.*, **28**, 51 (1934).
4. G. Gossrau, in: *Handbuch der Technischen Electrochemie*, 2nd ed., Vol. 3, *Technische Elektrolyse*, Geest und Portig, Leipzig, 1955, p. 443.

5.4.7.2. Formation of Organolead–Group-IIA Compounds

Compounds containing Pb–group-IIA bonds are not well characterized. Such species—usually R_3Pb derivatives—are prepared in solution; their existence is inferred from reaction products. Efforts to isolate them pure fail. They are thermolabile and air and moisture sensitive; precautions during synthesis, e.g., inert gas atmosphere and low T, must be taken. Stability decreases with increasing atomic number of the group-IIA element and aryl are more stable than alkyl. Donors exert a stabilizing effect and, therefore, solvents such as tetrahydrofuran (THF) or pyridine (PY) are expedient for preparation and handling them. Diethyl ether is not sufficiently basic to impart adequate stability. The reactivity can be correlated with ionic character in the Pb–group-IIA element bond, the organolead moiety being anionic.

Organolead–Mg compounds are used for in situ synthesis, e.g., for the preparation of unsymmetrical organolead compounds, $\text{R}_3\text{R}'\text{Pb}$.

(F. HUBER, K. GRÄTZ)

5.4. Formation of Bonds between Elements

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5.4.7. Formation of the Lead-Group-IIA Bond

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Compounds containing Pb-group-IIA bonds are not well characterized. Such species—usually R_3Pb derivatives—are prepared in solution; their existence is inferred from reaction products. Efforts to isolate them pure fail. They are thermolabile and air and moisture sensitive; precautions during synthesis, e.g., inert gas atmosphere and low T, must be taken. Stability decreases with increasing atomic number of the group-IIA element and aryl are more stable than alkyl. Donors exert a stabilizing effect and, therefore, solvents such as tetrahydrofuran (THF) or pyridine (PY) are expedient for preparation and handling them. Diethyl ether is not sufficiently basic to impart adequate stability. The reactivity can be correlated with ionic character in the Pb-group-IIA element bond, the organolead moiety being anionic.

Organolead-Mg compounds are used for in situ synthesis, e.g., for the preparation of unsymmetrical organolead compounds, $\text{R}_3\text{R}'\text{Pb}$.

(F. HUBER, K. GRÄTZ)

5.4. Formation of Bonds between Elements

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5.4.7. Formation of the Lead-Group-IIA Bond

5.4.7.2. Formation of Organolead-Group-IIA Compounds

A common procedure is the carbide process or carbide-thermal method in which CaC_2 either is reacted with molten Pb metal:



or is reduced, e.g., by Al in the presence of molten Pb metal in an inert or reducing atmosphere at ca. 1000°C in the presence of a flux²⁻⁵. The Ca metal formed during these reactions and Pb metal yield CaPb_3 and Ca-Pb alloy, the composition depending on the stoichiometry.

As the source of Ca instead of CaCl_2 or CaC_2 CaO can also be used. It is reduced by Al metal in the presence of CaCl_2 and NaCl (as flux) in molten Pb metal⁶.

(F. HUBER, K. GRÄTZ)

1. V. Aravamuthan, S. Visvanathan, *Chem. Age India*, **16**, 1033 (1965). A review.
2. K. Jellinek, G. Tomoff, *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.*, **111**, 234 (1924).
3. T. Yokoyama, S. Oka, K. Ozaki, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **55**, 64 (1952).
4. A. Ya. Nashelskii, *Nauch. Doklady Vysshei Shkoly, Met.*, No. 3, 47 (1958); *Chem. Abstr.*, **53**, 9954 (1959).
5. A. Ya. Nashelskii, *Izvest. Yysshikh Ucheb. Zavedenii, Tsvetnaya Met.*, No. 6, 72 (1958); *Chem. Abstr.*, **53**, 18,712 (1959).
6. M. Gramatikov, *Rudobodiv. Met.*, **20**, No. 12, 15 (1965); *Chem. Abstr.*, **65**, 420 (1966).
7. W.-S. Cheng, *K'o Hsueh Tung Pao*, No. 10, 40 (1962); *Chem. Abstr.*, **59**, 14966 (1963).

5.4.7.1.3. by Electrolysis.

The preparation of binary alloys of Pb and Mg^1 , Ca^{2-4} , Sr^4 or Ba^4 also can be performed by electrolysis of salt melts at a liq Pb metal cathode using fluorides as flux at ca. $700^\circ\text{--}800^\circ\text{C}$ and graphite anodes. In all cases air must be excluded.

(F. HUBER, K. GRÄTZ)

1. E. A. Ashcroft, *Trans. Faraday Soc.*, **14**, 273 (1919).
2. K. Sakai, *J. Electrochem. Soc. Jpn.*, **18**, 12 (1950); *Chem. Abstr.*, **45**, 3258 (1951).
3. W. Siecke, Ger. Pat. 584,399 (1933); *Chem. Abstr.*, **28**, 51 (1934).
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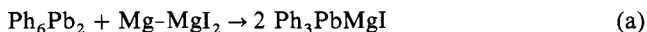
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Triphenylplumbyl-group-IIA compounds¹ are formed by Pb—Pb bond cleavage of Ph_6Pb_2 with an alkaline-earth metal in liq NH_3 . The presence of the triphenyllead metal species² is demonstrated by the formation of Ph_3PbR ($\text{R} = \text{C}_6\text{H}_5\text{CH}_2$, e.g.), when RCl is added to the resultant reaction mixture¹. Yields of $\text{Ph}_3\text{PbCH}_2\text{C}_6\text{H}_5$ are highest (80%) when Ca metal is used to cleave Ph_6Pb_2 ; with Sr and Ba metal yields of 70 and 58%, respectively, are obtained¹.

Lead-lead cleavage in some hexaorganodileads and formation of R_3PbMgI ($\text{R} = \text{C}_6\text{H}_5$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4$) is also accomplished with the binary Mg-MgI_2 system in ether-benzene at RT or on gentle heating:



Carboxylation with CO_2 authenticates this compound.

Other substituted hexaaryldileads ($\text{R} = 2\text{-CH}_3\text{OC}_6\text{H}_4$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) or cyclohexyldilead and Mg-MgI_2 do not react according to (a); they finally yield³ R_3PbI .

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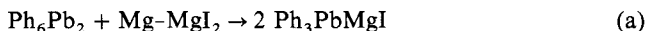
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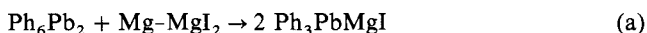
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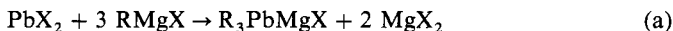
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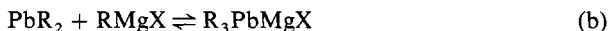
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Deeply colored solutions result that involve equilibrium mixtures⁵:



The $\text{R}_3\text{PbMgX} \cdot 2 \text{D}$ solvates are formed⁴ in which solvent molecules, D, coordinate to Mg. In such solvents as tetrahydrofuran (THF) or pyridine (py), but not in Et_2O , the stability is high enough to obtain stable solutions of R_3PbMgX ; for stabilizing trialkylleads, addition of hexamethylphosphoramide (HMPA) to the solvent THF is favorable¹¹. The stability of R_3PbMgX is also dependent on R. Solutions of compounds with voluminous ligands, such as $\text{Me}_3\text{SiCH}_2^8$ or mesityl⁵, at Pb are appreciably more stable than solutions of trialkylleads, R_3PbMgX .

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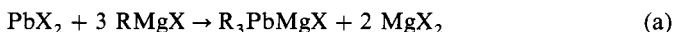
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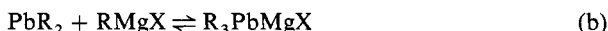
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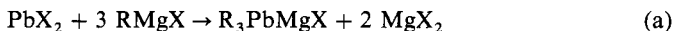
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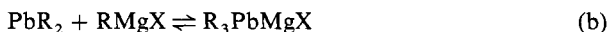
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Lead (II) halides react with organomagnesium halide reagents to yield R_4Pb and R_6Pb_2 . The R_3PbMgX are intermediates in this complex reaction^{1,2}. Taking advantage of the stabilizing effects of donors², R_3PbMgX ($\text{R} = \text{Me}^{2,3}$, Et^4 , $\text{X} = \text{Cl}$; $\text{R} = \text{Ph}^{5,6}$, $\text{X} = \text{Cl}$, Br ; $\text{R} = \text{Me}_3\text{CCH}_2^7$, $\text{Me}_3\text{SiCH}_2^8$, $\text{X} = \text{Cl}$; $\text{R} = \text{Me}_3\text{C}_6\text{H}_5^5$, $\text{PhC}(\text{C}=\text{CH}_2)\text{C}_6\text{H}_4^9$, $\text{X} = \text{Br}$) can be produced in solution or are presumed as intermediates ($\text{R} = \text{C}_6\text{F}_5^{10}$, $\text{X} = \text{Br}$), when PbX_2 reacts with organomagnesium-halide reagent in donor solvents:



Deeply colored solutions result that involve equilibrium mixtures⁵:



The $\text{R}_3\text{PbMgX} \cdot 2 \text{D}$ solvates are formed⁴ in which solvent molecules, D, coordinate to Mg. In such solvents as tetrahydrofuran (THF) or pyridine (py), but not in Et_2O , the stability is high enough to obtain stable solutions of R_3PbMgX ; for stabilizing trialkylleads, addition of hexamethylphosphoramide (HMPA) to the solvent THF is favorable¹¹. The stability of R_3PbMgX is also dependent on R. Solutions of compounds with voluminous ligands, such as $\text{Me}_3\text{SiCH}_2^8$ or mesityl⁵, at Pb are appreciably more stable than solutions of trialkylleads, R_3PbMgX .

As a typical example the preparation of Et_3PbMgCl is performed under N_2 in a three-necked flask, equipped with a cooler and a stirrer. First an organomagnesium-halide solution, e.g., from Mg metal and EtCl (small xs) in THF distilled over LiAlH_4 , is prepared; then, after xs EtCl is removed by heating under reflux for some minutes, ground PbCl_2 is added slowly at 5°C from a flask connected with the reaction vessel⁴. Stirring is continued until the PbCl_2 is dissolved. A greenish-brown solution containing Et_3PbMgCl forms.

The RMgX solution should be free of elementary Mg, because this reduces Pb(II) to Pb metal in the subsequent steps, lowering yields of R_3PbMgX ¹².

Instead of Pb(II) halides acetate can also be reacted⁴ with RMgX ($\text{X} = \text{halide}$) to obtain R_3PbMgX .

(F. HUBER, K. GRÄTZ)

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Abbreviations

abs	absolute
a.c.	alternating current
Ac	acetyl, CH_3CO
acac	acetylacetonate anion
acacH	acetylacetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
AcO	acetate anion, $\text{CH}_3\text{C}(\text{O})\text{O}$
Ad	adamantyl
ads	adsorbed
AIBN	2,2'-azobis(isobutyronitrile), $2,2'-[(\text{CH}_3)_2\text{CCN}]_2\text{N}_2$
Alk	alkyl
am	amine
amt	amount
Am	amyl, C_5H_{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
BBN	9-Borabicyclo[3.3.1]nonane
bcc	body-centered cubic
BD	butadiene
bipy	2,2'-bipyridyl
bipyH	protonated 2,2'-bipyridyl
bp	boiling point
Bu	butyl, C_4H_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
cf.	compare
Ch.	chapter
CHD	1,3-cycloheptadiene
Chx	cyclohexyl
ChxD	1,3-cyclohexadiene
COD	cyclooctadiene
conc	concentrated (not concentration)
const.	constant
COT	cyclooctatriene
Cp	cyclopentadienyl, C_5H_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-diaza butadiene
DBA	dibenzylideneacetone
d.c.	direct current
DCM	dicyclopentadienylmethane
DCME	$\text{Cl}_2\text{CHC}(\text{O})\text{CH}_3$
DCP	1,3-dicyclopentadienylpropane
DDT	dichlorodiphenyltrichloroethane, 1,1,1'-trichloro-2,2-bis-(4-chlorophenyl)ethane
dec	decomposed
DED	1,1-bis(ethoxycarbonyl)ethene-2,2-dithiolate, $[(\text{H}_3\text{C}_2\text{OC}(\text{O}))_2\text{C}=\text{CS}_2]^{2-}$
depe	1,2-bis(diphenylphosphino)ethene, $(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$
DIAD	diindenylanthracenyl
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, $[\text{H}_2\text{N}(\text{CH}_2)_2]_2\text{NH}$
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
DMA	dimethylacetamide
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, $\text{HC}(\text{O})\text{N}(\text{CH}_3)_2$
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, $1,2-(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$
dpmm	bis(diphenylphosphino)methane, $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CH}_2$
dppeoe	bis(diphenylphosphoryl)ethane
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, $[\text{HOC}(\text{O})]_2\text{N}(\text{CH}_2)_2\text{N}[\text{C}(\text{O})\text{OH}]_2$
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, CH_2CH_3
etc.	et cetera, and so forth
Et_2O	diethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$
EtOH	ethanol, $\text{C}_2\text{H}_5\text{OH}$
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, $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OCH}_3$
graph	graphite
GS	ground state
h	hour, hours
HD	1,5-hexadiene
Hex	hexyl
HMDB	hexamethyl(Dewar benzene)
hmde	hanging mercury drop electrode
HMI	heptamethylindenyl
HMPA	hexamethylphosphoramide, $[(\text{CH}_3)_2\text{N}]_3\text{PO}$
HOMO	highest occupied molecular orbital
i.e.	id est, that is
Im	imidazole
inter alia	among other things
IPC	isopinocampylborane
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_3
Men	menthyl
MeOH	methanol, CH_3OH
mer	meridional; the repeating unit of an oligomer or polymer
mhp	2-hydroxy-6-methylpyridine, 2-HO, 6- $\text{CH}_3\text{C}_5\text{H}_3\text{N}$
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, $\text{N}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_3$
Np	naphthyl
NPP	normal pulse polarography
NQR	nuclear quadrupole resonance
NTA	nitrilotriacetate
o	ortho
obs	observed
Oct	octyl
oep	octaethylporphyrin
OF	oxidation factor
O_h	octahedral
Oq	oxyquinolate
p	para
p.	page
P	pressure
Pat.	patent
pet.	petroleum
Ph	phenyl, C_6H_5
phen	1,10-phenanthroline
Ph_2PPy	2-(diphenylphosphino)pyridine, 2- $(\text{C}_6\text{H}_5)_2\text{PC}_5\text{H}_4\text{N}$
pip	piperidine, $\text{C}_5\text{H}_{10}\text{N}$
PMDT	pentamethyldiethylenetriamine, $(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$
PMR	proton magnetic resonance
pn	propylene-1,3-diamine, 1,3- $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
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
Sia	Diisamyl
soln	solution
solv	solvated
sp	specific
STP	standard temperature and pressure
subl	sublimes
Suppl.	supplement
sym	symmetrical, symmetric
t	time; tertiary
T	temperature
T_d	tetrahedral
TCNE	tetracyanoethylene
TEA	tetraethylammonium ion, $[(C_2H_5)_4N]^+$
terpy	2,2'2''-terpyridyl
tetraphos	$Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$
TGA	thermogravimetric analysis
TGL	triethyleneglycol dimethylether
THF	tetrahydrofuran
THP	tetrahydropyran
THT	tetrahydrothiophene
Thx	thexyl
TLC	thin-layer chromatography
TMED	N,N,N',N'-tetramethylethylenediamine, $(CH_3)_2N(CH_2)_2N(CH_3)_2$
TMPH	2,2,6,6-tetramethylpiperidine, 2,2,6,6-(CH_3) ₄ C ₅ H ₆ N
Tos	tosyl, tolylsulfonyl, 4- $CH_3C_6H_4SO_2$
TPA	tetraphenylarsonium ion, $[(C_6H_5)_4As]^+$

TPPO	triphenylphosphineoxide
triars	bis-[2-(dimethylarsino)phenyl]methylarsine, [2-(CH ₃) ₂ AsC ₆ H ₄] ₂ AsCH ₃
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane, [(C ₆ H ₅) ₂ PCH ₂] ₃ CCH ₃
trien	triethylenetetraamine, H ₂ N(CH ₂) ₂ NH(CH ₂) ₂ NH(CH ₂) ₂ NH ₂
UV	ultraviolet
v	vicinal
Vi	(E)-[2-(CH ₃) ₂ NCH ₂ C ₆ H ₄]C=C(CH ₃)C ₆ H ₄ CH ₃ -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

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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.

Al

Al

Formation of pure: 5.3.3.5.3

Reaction with C_6H_6/BX_3 : 5.3.2.3.3

Reaction with $Hg(GeR_3)_2$: 5.3.13.2

Reaction with $Hg(SiR_3)_2$: 5.3.8.3

Reaction with $Hg(SnR_3)_2$: 5.3.18.2

Reaction with RX : 5.3.3.2.2

Reaction with R_2Hg : 5.3.3.2.3

Reaction with R_3SiCl : 5.3.8.4

Reaction with F_3C : 5.3.3.2.2

Reaction with H_2 and R_3Al : 5.3.3.2.1

$AlBr * C_4H_{10}$

$AlBr_3$

$AlBr_3$

Activation of Al metal: 5.3.3.2.2

Reaction with $M-C$ bonds: 5.3.3.3.1

Redistribution: 5.3.3.3.2

- AlF_6Na_3
 $\text{Na}_3[\text{AlF}_6]$
 Formation: 5.3.3.3.2
 AlF_9^*C_6
 $\text{AlGaLi}_2^*\text{C}_{16}\text{H}_{40}$
 $\text{AlGeLi}^*\text{C}_8\text{H}_{14}$
 $\text{AlGeLi}^*\text{C}_{13}\text{H}_{16}$
 $\text{AlGeLi}^*\text{C}_{18}\text{H}_{18}$
 $\text{AlGe}_3\text{O}^*\text{C}_{13}\text{H}_{35}$
 AlH_3
 AlH_3
 Catalyst for MgH_2 addition to olefins:
 5.4.2.4.1
 Hydroalumination reagent: 5.3.3.4.1
 Reaction with $\text{Li}[\text{Ph}_3\text{Si}]$: 5.3.8.2.2
 Redistribution: 5.3.3.4.3
 AlH_4Li
 $\text{Li}[\text{AlH}_4]$
 Reaction with LiGeR_3 : 5.3.13.3
 Reaction with $\text{Li}[\text{Ph}_3\text{Si}]$: 5.3.8.2.2
 Reaction with Ph_6Si_2 : 5.3.8.7
 Reaction with RLi : 5.3.3.4.4
 Reaction with MgR_2 : 5.4.2.4.3
 Reaction with R_3Al : 5.3.3.4.3
 Reaction with R_3GeGeR_3 : 5.3.13.4
 Reaction with alkenes: 5.3.3.4.1
 Reaction with alkynes: 5.3.3.5.2
 Reactivity towards R_2M : 5.3.3.4.4
 Solvent drying: 5.4.2.2.1
 trans-hydroalumination: 5.3.3.4.1
 AlH_4Na
 $\text{Na}[\text{AlH}_4]$
 Hydroalumination of alkynes: 5.3.3.4.1
 Hydroalumination reagent: 5.3.3.4.1
 Reaction with $\text{Na}[\text{Et}_4\text{Al}]$: 5.3.3.4.3
 Reaction with R_3Al : 5.3.3.4.3
 Reaction with alkynes: 5.3.3.5.2
 Reaction with furane: 5.3.3.5.2
 Reaction with thiophene: 5.3.3.5.2
 $\text{AlI}^*\text{C}_4\text{H}_{10}$
 $\text{AlI}^*\text{C}_5\text{H}_{12}$
 AlI_3
 AlI_3
 Activation of Al metal: 5.3.3.2.2
 Redistribution: 5.3.3.3.2
 $\text{AlK}^*\text{C}_{10}\text{H}_{16}$
 $\text{AlKO}_3\text{Si}_4^*\text{C}_{24}\text{H}_{66}$
 $\text{AlKS}_4^*\text{C}_{12}\text{H}_{36}$
 $\text{AlLi}^*\text{C}_8\text{H}_{12}$
 $\text{AlLi}^*\text{C}_9\text{H}_{12}$
 $\text{AlLi}^*\text{C}_{12}\text{H}_{12}$
 $\text{AlLi}^*\text{C}_{12}\text{H}_{28}$
 $\text{AlLi}^*\text{C}_{24}\text{H}_{20}$
 $\text{AlLi}^*\text{C}_{32}\text{H}_{20}$
 $\text{AlLi}^*\text{C}_{32}\text{H}_{52}$
 $\text{AlLi}^*\text{C}_{56}\text{H}_{40}$
 $\text{AlLiO}_3\text{Si}_4^*\text{C}_{24}\text{H}_{66}$
 $\text{AlLiO}_4\text{Si}_4^*\text{C}_{28}\text{H}_{78}$
 $\text{AlLiSi}^*\text{C}_{11}\text{H}_{20}$
 $\text{AlLiSi}^*\text{C}_{18}\text{H}_{18}$
 $\text{AlLiSi}_4^*\text{C}_{12}\text{H}_{36}$
 $\text{AlLiSn}^*\text{C}_6\text{H}_{18}$
 $\text{AlLiSn}^*\text{C}_{15}\text{H}_{36}$
 $\text{AlLiSn}^*\text{C}_{18}\text{H}_{42}$
 $\text{AlLiZn}^*\text{C}_2\text{H}_{10}$
 $\text{AlMg}^*\text{C}_5\text{H}_{15}$
 $\text{AlN}^*\text{C}_2\text{H}_8$
 $\text{AlN}^*\text{C}_3\text{H}_6$
 $\text{AlN}^*\text{C}_3\text{H}_{12}$
 $\text{AlN}^*\text{C}_4\text{H}_{14}$
 $\text{AlN}^*\text{C}_5\text{H}_{10}$
 $\text{AlN}^*\text{C}_5\text{H}_{16}$
 $\text{AlN}^*\text{C}_5\text{H}_{16}$
 $\text{AlN}^*\text{C}_6\text{H}_{18}$
 $\text{AlN}^*\text{C}_7\text{H}_{20}$
 $\text{AlN}^*\text{C}_9\text{H}_{18}$
 $\text{AlN}^*\text{C}_9\text{H}_{18}$
 $\text{AlN}^*\text{C}_9\text{H}_{18}$
 $\text{AlN}^*\text{C}_9\text{H}_{24}$
 $\text{AlN}^*\text{C}_{10}\text{H}_{26}$
 $\text{AlN}^*\text{C}_{11}\text{H}_{14}$
 $\text{AlN}^*\text{C}_{12}\text{H}_{18}$
 $\text{AlN}^*\text{C}_{12}\text{H}_{30}$
 $\text{AlN}^*\text{C}_{14}\text{H}_{14}$
 $\text{AlN}^*\text{C}_{14}\text{H}_{16}$
 $\text{AlN}^*\text{C}_{25}\text{H}_{22}$
 $\text{AlN}^*\text{C}_{25}\text{H}_{22}$
 $\text{AlN}^*\text{C}_{27}\text{H}_{24}$
 $\text{AlN}^*\text{C}_{29}\text{H}_{20}$
 $\text{AlN}_2^*\text{C}_{12}\text{H}_{29}$
 $\text{AlNa}^*\text{C}_4\text{H}_{12}$
 $\text{AlNa}^*\text{C}_4\text{H}_{12}$
 $\text{AlNa}^*\text{C}_6\text{H}_{12}$
 $\text{AlNa}^*\text{C}_6\text{H}_{16}$
 $\text{AlNa}^*\text{C}_6\text{H}_{16}$
 $\text{AlNa}^*\text{C}_8\text{H}_{20}$
 $\text{AlNa}^*\text{C}_{12}\text{H}_{14}$
 $\text{AlNa}^*\text{C}_{12}\text{H}_{18}$
 $\text{AlNa}^*\text{C}_{12}\text{H}_{28}$
 $\text{AlNa}^*\text{C}_{24}\text{H}_{20}$
 $\text{AlNa}^*\text{C}_{24}\text{H}_{36}$
 $\text{AlNaO}_4^*\text{C}_6\text{H}_{15}$
 $\text{AlNaO}_4^*\text{C}_{16}\text{H}_{12}$
 $\text{AlNaO}_8\text{Si}_4^*\text{C}_{44}\text{H}_{116}$

- $\text{AlNaS}_4 \cdot \text{C}_{16}\text{H}_{12}$
 $\text{AlNaSi}_4 \cdot \text{C}_{12}\text{H}_{36}$
 $\text{AlNaSi}_4 \cdot \text{C}_{12}\text{H}_{36}$
 $\text{AlNaSi}_4 \cdot \text{C}_{26}\text{H}_{52}$
 $\text{AlO} \cdot \text{C}_4\text{H}_{11}$
 $\text{AlO} \cdot \text{C}_4\text{H}_{13}$
 $\text{AlO} \cdot \text{C}_7\text{H}_{15}$
 $\text{AlO} \cdot \text{C}_7\text{H}_{17}$
 $\text{AlO} \cdot \text{C}_7\text{H}_{19}$
 $\text{AlO} \cdot \text{C}_8\text{H}_{19}$
 $\text{AlO} \cdot \text{C}_{10}\text{H}_{13}$
 $\text{AlO} \cdot \text{C}_{10}\text{H}_{17}$
 $\text{AlO} \cdot \text{C}_{10}\text{H}_{19}$
 $\text{AlO} \cdot \text{C}_{10}\text{H}_{23}$
 $\text{AlO} \cdot \text{C}_{11}\text{H}_{19}$
 $\text{AlO} \cdot \text{C}_{12}\text{H}_{27}$
 $\text{AlO} \cdot \text{C}_{13}\text{H}_{19}$
 $\text{AlO} \cdot \text{C}_{13}\text{H}_{31}$
 $\text{AlO} \cdot \text{C}_{16}\text{H}_{37}$
 $\text{AlO} \cdot \text{C}_{19}\text{H}_{43}$
 $\text{AlO} \cdot \text{C}_{22}\text{H}_{25}$
 $\text{AlO} \cdot \text{C}_{28}\text{H}_{25}$
 $\text{AlO} \cdot \text{C}_{38}\text{H}_{35}$
 $\text{AlOSi}_3 \cdot \text{C}_{13}\text{H}_{35}$
 $\text{AlOSi}_3 \cdot \text{C}_{13}\text{H}_{35}$
 $\text{AlOSi}_3 \cdot \text{C}_{13}\text{H}_{37}$
 $\text{AlOSn}_3 \cdot \text{C}_{13}\text{H}_{35}$
 $\text{AlO}_2\text{Si} \cdot \text{C}_4\text{H}_{15}$
 $\text{AlO}_3 \cdot \text{C}_3\text{H}_9$
 $\text{AlPSi}_6 \cdot \text{C}_{18}\text{H}_{54}$
 $\text{AlSb} \cdot \text{C}_{16}\text{H}_{40}$
 $\text{AlSi} \cdot \text{C}_8\text{H}_{21}$
 $\text{AlSi} \cdot \text{C}_{12}\text{H}_{21}$
 $\text{AlSi} \cdot \text{C}_{22}\text{H}_{25}$
 $\text{AlSi}_2 \cdot \text{C}_{38}\text{H}_{35}$
 $\text{AlSi}_3 \cdot \text{C}_9\text{H}_{27}$
 $\text{AlSi}_3 \cdot \text{C}_{12}\text{H}_{33}$
 $\text{AlSi}_3 \cdot \text{C}_{15}\text{H}_{39}$
 $\text{AlSi}_3 \cdot \text{C}_{54}\text{H}_{45}$
 $\text{AlSn} \cdot \text{C}_7\text{H}_{19}$
 $\text{AlSn} \cdot \text{C}_{16}\text{H}_{37}$
 $\text{AlSr} \cdot \text{C}_8\text{H}_{20}$
 $\text{Al}_2\text{Ba} \cdot \text{C}_{12}\text{H}_{32}$
 $\text{Al}_2\text{Ba} \cdot \text{C}_{16}\text{H}_{40}$
 $\text{Al}_2\text{Be} \cdot \text{C}_8\text{H}_{24}$
 $\text{Al}_2\text{Be} \cdot \text{C}_{16}\text{H}_{24}$
 $\text{Al}_2\text{Br}_3 \cdot \text{C}_3\text{H}_9$
 $\text{Al}_2\text{Br}_3 \cdot \text{C}_6\text{H}_{15}$
 $\text{Al}_2\text{Br}_3 \cdot \text{C}_9\text{H}_{15}$
 $\text{Al}_2\text{Br}_3 \cdot \text{C}_{18}\text{H}_{15}$
 $\text{Al}_2 \cdot \text{C}_6\text{H}_{18}$
 $\text{Al}_2 \cdot \text{C}_6\text{H}_{18}$
 $\text{Al}_2 \cdot \text{C}_{10}\text{H}_{18}$
 $\text{Al}_2 \cdot \text{C}_{12}\text{H}_{30}$
 $\text{Al}_2 \cdot \text{C}_{24}\text{H}_{54}$
 $\text{Al}_2 \cdot \text{C}_{84}\text{H}_{60}$
 $\text{Al}_2\text{Ca} \cdot \text{C}_{16}\text{H}_{40}$
 $\text{Al}_2\text{Ca} \cdot \text{C}_{16}\text{H}_{40}$
 $\text{Al}_2\text{Cl}_3 \cdot \text{C}_3\text{H}_9$
 $\text{Al}_2\text{Cl}_3 \cdot \text{C}_3\text{H}_9$
 $\text{Al}_2\text{Cl}_3 \cdot \text{C}_6\text{H}_{15}$
 $\text{Al}_2\text{Cl}_3 \cdot \text{C}_6\text{H}_{15}$
 $\text{Al}_2\text{Cl}_3 \cdot \text{C}_{18}\text{H}_{15}$
 $\text{Al}_2\text{Cl}_4 \cdot \text{CH}_2$
 $\text{Al}_2\text{I}_3 \cdot \text{C}_3\text{H}_9$
 $\text{Al}_2\text{I}_3 \cdot \text{C}_6\text{H}_{15}$
 $\text{Al}_2\text{I}_3 \cdot \text{C}_{12}\text{H}_{27}$
 $\text{Al}_2\text{I}_3 \cdot \text{C}_{18}\text{H}_{15}$
 $\text{Al}_2\text{I}_3 \cdot \text{C}_{24}\text{H}_{51}$
 $\text{Al}_2\text{Mg} \cdot \text{C}_8\text{H}_{24}$
 $\text{Al}_2\text{N}_2 \cdot \text{C}_{22}\text{H}_{50}$
 $\text{Al}_2\text{N}_2\text{P}_2\text{Si} \cdot \text{C}_{14}\text{H}_{42}$
 $\text{Al}_2\text{N}_2\text{Si}_6 \cdot \text{C}_{24}\text{H}_{70}$
 $\text{Al}_2\text{Na} \cdot \text{C}_4\text{H}_{14}$
 $\text{Al}_2\text{Na}_2 \cdot \text{C}_{14}\text{H}_{30}$
 $\text{Al}_2\text{Na}_2 \cdot \text{C}_{26}\text{H}_{54}$
 $\text{Al}_2\text{Sb} \cdot \text{C}_{22}\text{H}_{55}$
 $\text{Al}_2\text{Sn}_2\text{Sr}_3$
 $\text{Sr}_3\text{Al}_2\text{Sn}_2$
 Formation: 5.4.6.1
 $\text{Al}_2\text{Sr} \cdot \text{C}_{16}\text{H}_{40}$
 $\text{Al}_3 \cdot \text{C}_8\text{H}_{21}$
 $\text{Al}_3\text{Cl}_6\text{Ga} \cdot \text{C}_{12}\text{H}_{30}$
 $\text{Al}_4 \cdot \text{C}_3$
 $\text{Al}_4\text{O}_4 \cdot \text{C}_{40}\text{H}_{74}$
 $\text{Al}_6 \cdot \text{C}_{14}\text{H}_{30}$
 $\text{As} \cdot \text{C}_5\text{H}_{15}$
 $\text{AsCl}_3\text{Sn} \cdot \text{C}_{24}\text{H}_{20}$
 $\text{AsGa} \cdot \text{C}_8\text{H}_{24}$
 As_2B_{12}
 B_{12}As_2
 Formation: 5.3.2.1
B
B
 Formation: 5.3.2.1.1
 Reaction with BCl_3 and H_2 : 5.3.2.2.8
 Reaction with B_4C : 5.3.2.2.1
 Reaction with SiO_2 : 5.3.7.1
 Reaction with SiF_4 : 5.3.7.2
 Reaction with elemental carbon:
 5.3.2.1.1, 5.3.2.2.1
 $\text{BBa} \cdot \text{C}_8\text{H}_{20}$
 $\text{BBr} \cdot \text{C}_2\text{H}_6$
 $\text{BBr} \cdot \text{C}_4\text{H}_{10}$

- $\text{BBr}^*\text{C}_7\text{H}_8$
 $\text{BBr}^*\text{C}_8\text{H}_{18}$
 $\text{BBr}^*\text{C}_{12}\text{H}_{10}$
 $\text{BBrF}_4^*\text{C}_{12}\text{H}_{10}$
 $\text{BBrS}^*\text{C}_2\text{H}_8$
 $\text{BBr}_2^*\text{CH}_3$
 $\text{BBr}_2^*\text{C}_2\text{H}_3$
 $\text{BBr}_2^*\text{C}_2\text{H}_5$
 $\text{BBr}_2^*\text{C}_6\text{H}_5$
 $\text{BBr}_2^*\text{C}_{13}\text{H}_{11}$
 $\text{BBr}_2\text{ClS}^*\text{C}_7\text{H}_{14}$
 $\text{BBr}_2\text{Fe}^*\text{C}_{10}\text{H}_9$
 $\text{BBr}_2\text{MnO}_3^*\text{C}_8\text{H}_4$
 $\text{BBr}_2\text{MnO}_3^*\text{C}_9\text{H}_6$
 $\text{BBr}_2\text{P}_6\text{Sn}^*\text{C}_{81}\text{H}_{81}$
 $\text{BBr}_2\text{S}^*\text{C}_2\text{H}_7$
 $\text{BBr}_2\text{S}^*\text{C}_8\text{H}_{17}$
 $\text{BBr}_2\text{S}^*\text{C}_8\text{H}_{19}$
 BBr_3
 BBr_3
 Addition to alkynes: 5.3.2.3.4
 Addition to olefines: 5.3.2.3.4
 Cleavage of $\text{M}-\text{C}$: 5.3.2.3.1
 Reaction with $\text{h}^5\text{-C}_5\text{H}_5-\text{M}$: 5.3.2.3.3
 Reaction with $(\text{C}_6\text{H}_5)_2\text{CH}_2$: 5.3.2.3.3
 Reaction with CCl_4 and H_2 : 5.3.2.2.3
 Reaction with CH_4 and H_2 : 5.3.2.2.3
 Reaction with C_6H_6 : 5.3.2.3.3
 Redistribution: 5.3.2.3.6
 $\text{BBr}_3^*\text{C}_8\text{H}_6$
 B^*CH_3
 $\text{B}^*\text{C}_3\text{H}_9$
 $\text{B}^*\text{C}_4\text{H}_{11}$
 $\text{B}^*\text{C}_6\text{H}_{13}$
 $\text{B}^*\text{C}_6\text{H}_{15}$
 $\text{B}^*\text{C}_6\text{H}_{15}$
 $\text{B}^*\text{C}_6\text{H}_{15}$
 $\text{B}^*\text{C}_8\text{H}_{17}$
 $\text{B}^*\text{C}_9\text{H}_{15}$
 $\text{B}^*\text{C}_9\text{H}_{17}$
 $\text{B}^*\text{C}_9\text{H}_{19}$
 $\text{B}^*\text{C}_9\text{H}_{21}$
 $\text{B}^*\text{C}_{10}\text{H}_{13}$
 $\text{B}^*\text{C}_{10}\text{H}_{19}$
 $\text{B}^*\text{C}_{10}\text{H}_{23}$
 $\text{B}^*\text{C}_{11}\text{H}_{15}$
 $\text{B}^*\text{C}_{11}\text{H}_{19}$
 $\text{B}^*\text{C}_{12}\text{H}_{11}$
 $\text{B}^*\text{C}_{12}\text{H}_{16}$
 $\text{B}^*\text{C}_{12}\text{H}_{21}$
 $\text{B}^*\text{C}_{12}\text{H}_{23}$
 $\text{B}^*\text{C}_{12}\text{H}_{27}$
 $\text{B}^*\text{C}_{12}\text{H}_{27}$
 $\text{B}^*\text{C}_{12}\text{H}_{27}$
 $\text{B}^*\text{C}_{12}\text{H}_{27}$
 $\text{B}^*\text{C}_{13}\text{H}_{23}$
 $\text{B}^*\text{C}_{13}\text{H}_{25}$
 $\text{B}^*\text{C}_{14}\text{H}_{19}$
 $\text{B}^*\text{C}_{14}\text{H}_{23}$
 $\text{B}^*\text{C}_{15}\text{H}_{25}$
 $\text{B}^*\text{C}_{15}\text{H}_{27}$
 $\text{B}^*\text{C}_{15}\text{H}_{33}$
 $\text{B}^*\text{C}_{16}\text{H}_{27}$
 $\text{B}^*\text{C}_{16}\text{H}_{29}$
 $\text{B}^*\text{C}_{16}\text{H}_{31}$
 $\text{B}^*\text{C}_{18}\text{H}_{15}$
 $\text{B}^*\text{C}_{18}\text{H}_{15}$
 $\text{B}^*\text{C}_{18}\text{H}_{33}$
 $\text{B}^*\text{C}_{18}\text{H}_{37}$
 $\text{B}^*\text{C}_{20}\text{H}_{35}$
 $\text{B}^*\text{C}_{21}\text{H}_{21}$
 $\text{B}^*\text{C}_{21}\text{H}_{33}$
 $\text{B}^*\text{C}_{24}\text{H}_{27}$
 $\text{B}^*\text{C}_{24}\text{H}_{47}$
 $\text{B}^*\text{C}_{30}\text{H}_{21}$
 $\text{B}^*\text{C}_{30}\text{H}_{51}$
 $\text{B}^*\text{C}_{36}\text{H}_{69}$
 $\text{BCa}^*\text{C}_8\text{H}_{20}$
 $\text{BCl}^*\text{C}_2\text{H}_6$
 $\text{BCl}^*\text{C}_4\text{H}_6$
 $\text{BCl}^*\text{C}_4\text{H}_8$
 $\text{BCl}^*\text{C}_4\text{H}_{10}$
 $\text{BCl}^*\text{C}_4\text{H}_{10}$
 $\text{BCl}^*\text{C}_5\text{H}_{10}$
 $\text{BCl}^*\text{C}_6\text{H}_{12}$
 $\text{BCl}^*\text{C}_6\text{H}_{14}$
 $\text{BCl}^*\text{C}_8\text{H}_{18}$
 $\text{BCl}^*\text{C}_9\text{H}_9$
 $\text{BCl}^*\text{C}_{10}\text{H}_{18}$
 $\text{BCl}^*\text{C}_{12}\text{H}_{10}$
 $\text{BCl}^*\text{C}_{12}\text{H}_{26}$
 $\text{BClF}_4^*\text{C}_{12}\text{H}_{10}$
 $\text{BClF}_4\text{N}_2^*\text{C}_6\text{H}_4$
 $\text{BClF}_6^*\text{C}_4$
 $\text{BCIN}^*\text{C}_4\text{H}_{10}$
 $\text{BCIN}^*\text{C}_6\text{H}_{15}$
 $\text{BCINSn}^*\text{C}_7\text{H}_{19}$
 $\text{BCIN}_2^*\text{C}_2\text{H}_4$
 $\text{BCIN}_2^*\text{C}_3\text{H}_6$
 $\text{BCIN}_2^*\text{C}_4\text{H}_{10}$
 $\text{BCIN}_2^*\text{C}_4\text{H}_{12}$
 $\text{BCIN}_2^*\text{C}_4\text{H}_{12}$
 $\text{BCIN}_2^*\text{C}_8\text{H}_{20}$
 $\text{BClO}^*\text{C}_4\text{H}_{10}$
 $\text{BClO}^*\text{C}_4\text{H}_{12}$

$\text{BClO}^*\text{C}_4\text{H}_{12}$
 $\text{BClO}_2^*\text{C}_2\text{H}_4$
 $\text{BClO}_2^*\text{C}_2\text{H}_6$
 $\text{BClO}_2^*\text{C}_2\text{H}_6$
 $\text{BCIS}^*\text{C}_2\text{H}_8$
 $\text{BCIS}^*\text{C}_8\text{H}_{20}$
 $\text{BCl}_2^*\text{CH}_3$
 $\text{BCl}_2^*\text{C}_2\text{H}_3$
 $\text{BCl}_2^*\text{C}_2\text{H}_5$
 $\text{BCl}_2^*\text{C}_2\text{H}_5$
 $\text{BCl}_2^*\text{C}_3\text{H}_5$
 $\text{BCl}_2^*\text{C}_3\text{H}_7$
 $\text{BCl}_2^*\text{C}_6\text{H}_5$
 $\text{BCl}_2^*\text{C}_6\text{H}_5$
 $\text{BCl}_2^*\text{C}_6\text{H}_5$
 $\text{BCl}_2^*\text{C}_6\text{H}_7$
 $\text{BCl}_2^*\text{C}_6\text{H}_{13}$
 $\text{BCl}_2^*\text{C}_8\text{H}_{17}$
 $\text{BCl}_2\text{F}_4\text{Ti}^*\text{C}_{12}\text{H}_8$
 $\text{BCl}_2\text{N}^*\text{C}_3\text{H}_6$
 $\text{BCl}_2\text{O}^*\text{C}_4\text{H}_{11}$
 $\text{BCl}_2\text{O}_2^*\text{CH}_3$
 $\text{BCl}_2\text{S}^*\text{C}_2\text{H}_7$
 $\text{BCl}_2\text{S}^*\text{C}_4\text{H}_3$
 $\text{BCl}_2\text{S}^*\text{C}_{10}\text{H}_{23}$
 BCl_3

BCl_3

Addition to alkynes: 5.3.2.3.4
 Addition to olefines: 5.3.2.3.4
 Cleavage of $\text{M}-\text{C}$: 5.3.2.3.1
 Formation: 5.3.2.2.2
 Reaction with $\text{HBX}_2 \cdot \text{Base}$: 5.3.2.5.1
 Reaction with SiX_2 : 5.3.7.2
 Reaction with SiC : 5.3.7.1
 Reaction with CCl_4 and H_2 : 5.3.2.2.3
 Reaction with CO and H_2 : 5.3.2.2.2
 Reaction with CH_4 : 5.3.2.2.5
 Reaction with CH_4 and H_2 : 5.3.2.2.3
 Reaction with C_6H_6 : 5.3.2.3.3
 Reaction with elemental boron and H_2 :
 5.3.2.2.8
 Reaction with elemental carbon and H_2 :
 5.3.2.2.2
 Redistribution: 5.3.2.3.6
 Redistribution with R_3B : 5.3.2.6.1

$\text{BCl}_3^*\text{C}_2\text{H}_2$

$\text{BCl}_3^*\text{C}_6\text{H}_6$

$\text{BCl}_3^*\text{C}_{18}\text{H}_{12}$

BCl_5Si

$\text{Cl}_3\text{SiBCl}_2$

Formation: 5.3.7.2

$\text{BCo}^*\text{C}_{16}\text{H}_{15}$

BF

BF

Addition to alkynes: 5.3.2.3.4

Formation: 5.3.7.2

BF_2^*CH_3

$\text{BF}_2^*\text{C}_2\text{H}$

$\text{BF}_2^*\text{C}_2\text{H}_3$

$\text{BF}_2^*\text{C}_2\text{H}_5$

BF₃

BF₃

Addition to thallating agents: 5.3.6.3.4

Cleavage of $\text{M}-\text{C}$: 5.3.2.3.1

Reaction with AlR_3 : 5.3.3.3.2

Reaction with $[(\text{C}_6\text{H}_5)_4\text{As}][\text{SnCl}_3]$:
 5.3.17.4

Reaction with $(\text{CH}_3)_2\text{O} \cdot \text{B}_3\text{H}_7$ and CO :
 5.3.2.7.5

Reaction with SiX_2 : 5.3.7.2

Reaction with $[(\text{CH}_3)_2\text{N}]_2\text{Sn}$: 5.3.17.4

Reaction with $(\text{C}_2\text{H}_5)_2\text{Sn}$: 5.3.17.4

Reaction with CH_2N_2 : 5.3.2.3.5

Redistribution: 5.3.2.3.6

BF_3^*CH_2

$\text{BF}_3\text{O}^*\text{C}_4\text{H}_{10}$

$\text{BF}_4\text{I}^*\text{C}_{12}\text{H}_{10}$

BF₄K

$\text{K}[\text{BF}_4]$

Reaction with R_3Al : 5.3.2.3.1

Reaction with $\text{K}_2[\text{SiF}_6]$: 5.3.7.1

$\text{BF}_4\text{N}_2^*\text{C}_6\text{H}_5$

$\text{BF}_4\text{N}_2^*\text{C}_7\text{H}_7$

$\text{BF}_4\text{N}_2^*\text{C}_8\text{H}_9$

$\text{BF}_4\text{N}_2\text{O}^*\text{C}_7\text{H}_7$

$\text{BF}_4\text{N}_2\text{O}^*\text{C}_8\text{H}_9$

$\text{BF}_4\text{O}^*\text{C}_6\text{H}_{15}$

$\text{BF}_4\text{O}_2\text{Ti}^*\text{C}_{14}\text{H}_{14}$

$\text{BF}_4\text{O}_2\text{Ti}^*\text{C}_{16}\text{H}_{18}$

$\text{BF}_4\text{Ti}^*\text{C}_{12}\text{H}_{10}$

$\text{BF}_4\text{Ti}^*\text{C}_{14}\text{H}_{14}$

$\text{BF}_4\text{Ti}^*\text{C}_{16}\text{H}_{18}$

BF₇Si₂

$\text{F}_3\text{SiSiF}_2\text{BF}_2$

Formation: 5.3.7.2

BF₉Si₃

$\text{F}_3\text{Si}(\text{SiF}_2)_2\text{BF}_2$

Formation: 5.3.7.2

BF₁₁Si₄

$\text{Si}_4\text{BF}_{11}$

Formation: 5.3.7.2

BF₁₃Si₅

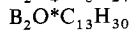
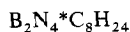
$\text{Si}_5\text{BF}_{13}$

Formation: 5.3.7.2

- $\text{BFeI}^*\text{C}_{11}\text{H}_{12}$
 $\text{BFeI}^*\text{C}_{16}\text{H}_{14}$
 $\text{BFeI}_2^*\text{C}_{10}\text{H}_9$
 BGeH_6K
 $\text{K}[\text{H}_3\text{GeBH}_3]$
 Formation: 5.3.12.2.2
 $\text{BGeLi}^*\text{C}_{36}\text{H}_{30}$
 BH_3
 BH_3
 Hydroboration reagent: 5.3.2.6.1
 Reaction with R_3SnLi : 5.3.17.2.1
 BH_3O_3
 $\text{B}(\text{OH})_3$
 Reaction with acetylene black or sugar:
 5.3.2.2.4
 $\text{BI}^*\text{C}_2\text{H}_6$
 $\text{BI}^*\text{C}_4\text{H}_{10}$
 $\text{BI}^*\text{C}_{10}\text{H}_{18}$
 $\text{BI}^*\text{C}_{12}\text{H}_{10}$
 $\text{BI}^*\text{C}_{12}\text{H}_{26}$
 $\text{BIMnO}_3^*\text{C}_9\text{H}_7$
 $\text{BIMnO}_3^*\text{C}_{10}\text{H}_9$
 $\text{BIMnO}_3^*\text{C}_{14}\text{H}_9$
 $\text{BIMnO}_3^*\text{C}_{15}\text{H}_{11}$
 $\text{BIS}^*\text{C}_2\text{H}_8$
 BI_2^*CH_3
 $\text{BI}_2^*\text{C}_2\text{H}_5$
 $\text{BI}_2^*\text{C}_4\text{H}_9$
 $\text{BI}_2^*\text{C}_6\text{H}_5$
 $\text{BI}_2^*\text{C}_6\text{H}_5$
 $\text{BI}_2\text{MnO}_3^*\text{C}_8\text{H}_4$
 $\text{BI}_2\text{MnO}_3^*\text{C}_9\text{H}_6$
 $\text{BI}_2\text{S}^*\text{C}_2\text{H}_7$
 BI_3
 BI_3
 Addition to alkynes: 5.3.2.3.4
 Addition to olefines: 5.3.2.3.4
 Cleavage of $\text{M}-\text{C}$: 5.3.2.3.1
 Halogen exchange: 5.3.2.3.1
 Reaction with $\text{h}^5\text{-C}_5\text{H}_5-\text{M}$: 5.3.2.3.3
 Reaction with Cl_4 : 5.3.2.2.3
 Reaction with C_6H_6 : 5.3.2.3.3
 Redox reactions: 5.3.2.3.3
 $\text{BI}_3^*\text{C}_6\text{H}_{10}$
 $\text{BI}_3^*\text{C}_8\text{H}_6$
 $\text{BK}^*\text{C}_8\text{H}_{18}$
 $\text{BKO}_3^*\text{C}_9\text{H}_{22}$
 $\text{BLi}^*\text{C}_6\text{H}_8$
 $\text{BLi}^*\text{C}_9\text{H}_{19}$
 $\text{BLiO}_2^*\text{C}_{20}\text{H}_{28}$
 $\text{BLiSi}^*\text{C}_{36}\text{H}_{30}$
 $\text{BLiSi}_2^*\text{C}_{14}\text{H}_{32}$
 $\text{BLiSi}_4^*\text{C}_{12}\text{H}_{36}$
 $\text{BLiSn}^*\text{C}_3\text{H}_{12}$
 $\text{BN}^*\text{C}_4\text{H}_6$
 $\text{BN}^*\text{C}_5\text{H}_{14}$
 $\text{BN}^*\text{C}_{11}\text{H}_{16}$
 $\text{BN}^*\text{C}_{14}\text{H}_{16}$
 $\text{BN}^*\text{C}_{17}\text{H}_{16}$
 $\text{BNO}^*\text{C}_{14}\text{H}_{16}$
 $\text{BNO}^*\text{C}_{16}\text{H}_{22}$
 $\text{BNSi}^*\text{C}_{24}\text{H}_{30}$
 $\text{BNSi}^*\text{C}_{40}\text{H}_{42}$
 $\text{BNSi}_4^*\text{C}_{50}\text{H}_{46}$
 $\text{BNSn}_2^*\text{C}_{10}\text{H}_{28}$
 $\text{BN}_2\text{O}_3\text{Si}^*\text{C}_{13}\text{H}_{33}$
 $\text{BN}_2\text{Pb}^*\text{C}_7\text{H}_{19}$
 $\text{BN}_2\text{Si}^*\text{C}_7\text{H}_{21}$
 $\text{BN}_2\text{Si}^*\text{C}_{22}\text{H}_{27}$
 $\text{BN}_2\text{Sn}^*\text{C}_6\text{H}_{15}$
 $\text{BN}_2\text{Sn}^*\text{C}_{11}\text{H}_{29}$
 $\text{BN}_3^*\text{C}_6\text{H}_{18}$
 $\text{BNa}^*\text{C}_6\text{H}_{16}$
 $\text{BNa}^*\text{C}_9\text{H}_{18}$
 $\text{BNa}^*\text{C}_{24}\text{H}_{20}$
 BO^*CH_3
 $\text{BO}^*\text{C}_4\text{H}_{11}$
 $\text{BO}^*\text{C}_5\text{H}_{11}$
 $\text{BO}^*\text{C}_7\text{H}_{15}$
 $\text{BO}^*\text{C}_9\text{H}_{17}$
 $\text{BO}^*\text{C}_9\text{H}_{21}$
 $\text{BO}^*\text{C}_{11}\text{H}_{25}$
 $\text{BO}^*\text{C}_{12}\text{H}_{11}$
 $\text{BO}^*\text{C}_{12}\text{H}_{17}$
 $\text{BO}^*\text{C}_{13}\text{H}_{21}$
 $\text{BO}^*\text{C}_{14}\text{H}_{15}$
 $\text{BO}^*\text{C}_{14}\text{H}_{23}$
 $\text{BO}^*\text{C}_{15}\text{H}_{25}$
 $\text{BO}^*\text{C}_{16}\text{H}_{19}$
 $\text{BO}^*\text{C}_{18}\text{H}_{35}$
 $\text{BO}^*\text{C}_{20}\text{H}_{15}$
 $\text{BOS}^*\text{C}_4\text{H}_{11}$
 $\text{BOS}^*\text{C}_6\text{H}_5$
 $\text{BO}_2^*\text{C}_2\text{H}_5$
 $\text{BO}_2^*\text{C}_3\text{H}_7$
 $\text{BO}_2^*\text{C}_3\text{H}_9$
 $\text{BO}_2^*\text{C}_4\text{H}_7$
 $\text{BO}_2^*\text{C}_4\text{H}_{11}$
 $\text{BO}_2^*\text{C}_6\text{H}_5$
 $\text{BO}_2^*\text{C}_6\text{H}_{13}$
 $\text{BO}_2^*\text{C}_7\text{H}_9$
 $\text{BO}_2^*\text{C}_7\text{H}_{15}$
 $\text{BO}_2^*\text{C}_8\text{H}_{17}$
 $\text{BO}_2^*\text{C}_8\text{H}_{19}$

$\text{BO}_2^*\text{C}_9\text{H}_{15}$
 $\text{BO}_2^*\text{C}_{10}\text{H}_{19}$
 $\text{BO}_2^*\text{C}_{10}\text{H}_{21}$
 $\text{BO}_2^*\text{C}_{11}\text{H}_{21}$
 $\text{BO}_2^*\text{C}_{12}\text{H}_{15}$
 $\text{BO}_2^*\text{C}_{12}\text{H}_{21}$
 $\text{BO}_2^*\text{C}_{12}\text{H}_{25}$
 $\text{BO}_2^*\text{C}_{13}\text{H}_{17}$
 $\text{BO}_2^*\text{C}_{14}\text{H}_{23}$
 $\text{BO}_2^*\text{C}_{14}\text{H}_{23}$
 $\text{BO}_2^*\text{C}_{16}\text{H}_{25}$
 $\text{BO}_2^*\text{C}_{17}\text{H}_{25}$
 $\text{BO}_2\text{S}^*\text{C}_4\text{H}_7$
 $\text{BO}_3^*\text{C}_3\text{H}_9$
 $\text{BO}_3^*\text{C}_3\text{H}_9$
 $\text{BO}_3^*\text{C}_4\text{H}_5$
 $\text{BO}_3^*\text{C}_6\text{H}_7$
 $\text{BO}_3^*\text{C}_6\text{H}_{15}$
 $\text{BO}_3^*\text{C}_8\text{H}_{17}$
 $\text{BO}_3^*\text{C}_{12}\text{H}_{27}$
 $\text{BS}^*\text{C}_2\text{H}_9$
 $\text{BS}^*\text{C}_4\text{H}_{11}$
 $\text{BSi}^*\text{C}_{12}\text{H}_{15}$
 $\text{BSi}^*\text{C}_{13}\text{H}_{27}$
 $\text{BSi}^*\text{C}_{24}\text{H}_{29}$
 $\text{BSi}_2^*\text{C}_{12}\text{H}_{31}$
 $\text{BSi}_3^*\text{C}_{12}\text{H}_{33}$
 $\text{BSr}^*\text{C}_8\text{H}_{20}$
 B_2BeH_8
 $\text{Be}(\text{BH}_4)_2$
 Reaction with ZnMe_2 : 5.4.3.3.1
 $\text{B}_2\text{BeO}_2\text{P}_4^*\text{C}_{10}\text{H}_{32}$
 $\text{B}_2\text{BeP}_4^*\text{C}_{12}\text{H}_{36}$
 $\text{B}_2\text{Be}_2^*\text{C}_2\text{H}_{14}$
 $\text{B}_2\text{Br}_2\text{P}_8\text{Sn}^*\text{C}_{105}\text{H}_{99}$
 B_2Br_4
 B_2Br_4
 Formation: 5.3.2.3.4
 $\text{B}_2\text{Br}_4^*\text{C}_5\text{H}_4$
 $\text{B}_2\text{Br}_4\text{CoP}_4^*\text{C}_{52}\text{H}_{48}$
 $\text{B}_2\text{Br}_4\text{Fe}^*\text{C}_{10}\text{H}_8$
 B_2^*CH_8
 $\text{B}_2^*\text{C}_2\text{H}_{10}$
 $\text{B}_2^*\text{C}_3\text{H}_{12}$
 $\text{B}_2^*\text{C}_4\text{H}_6$
 $\text{B}_2^*\text{C}_4\text{H}_{14}$
 $\text{B}_2^*\text{C}_5\text{H}_8$
 $\text{B}_2^*\text{C}_6\text{H}_{10}$
 $\text{B}_2^*\text{C}_6\text{H}_{18}$
 $\text{B}_2^*\text{C}_6\text{H}_{18}$
 $\text{B}_2^*\text{C}_8\text{H}_{22}$
 $\text{B}_2^*\text{C}_{10}\text{H}_{22}$

$\text{B}_2^*\text{C}_{12}\text{H}_{14}$
 $\text{B}_2^*\text{C}_{12}\text{H}_{24}$
 $\text{B}_2^*\text{C}_{12}\text{H}_{26}$
 $\text{B}_2^*\text{C}_{12}\text{H}_{28}$
 $\text{B}_2^*\text{C}_{12}\text{H}_{30}$
 $\text{B}_2^*\text{C}_{13}\text{H}_{28}$
 $\text{B}_2^*\text{C}_{15}\text{H}_{30}$
 $\text{B}_2^*\text{C}_{16}\text{H}_{30}$
 $\text{B}_2^*\text{C}_{16}\text{H}_{30}$
 $\text{B}_2^*\text{C}_{16}\text{H}_{38}$
 $\text{B}_2^*\text{C}_{18}\text{H}_{30}$
 $\text{B}_2^*\text{C}_{20}\text{H}_{46}$
 B_2Cl_4
 B_2Cl_4
 Addition to alkynes: 5.3.2.3.4
 Addition to cyclopropane: 5.3.2.3.4
 Addition to naphthalene: 5.3.2.3.4
 Addition to olefines: 5.3.2.3.4
 Formation: 5.3.2.3.4
 $\text{B}_2\text{Cl}_4^*\text{C}_2\text{H}_2$
 $\text{B}_2\text{Cl}_4^*\text{C}_3\text{H}_6$
 $\text{B}_2\text{Cl}_4^*\text{C}_6\text{H}_{10}$
 $\text{B}_2\text{Cl}_6^*\text{C}_2$
 $\text{B}_2\text{CoLi}^*\text{C}_8\text{H}_5$
 $\text{B}_2\text{CoP}_4^*\text{C}_{76}\text{H}_{68}$
 $\text{B}_2\text{F}_2^*\text{C}_8\text{H}_{12}$
 B_2F_4
 B_2F_4
 Addition to alkynes: 5.3.2.3.4
 Reaction with Si: 5.3.7.2
 $\text{B}_2\text{F}_4^*\text{C}_2\text{H}_2$
 $\text{B}_2\text{F}_6\text{Si}$
 $\text{F}_2\text{Si}(\text{BF}_2)_2$
 Formation: 5.3.7.2
 $\text{B}_2\text{FeI}_4^*\text{C}_{10}\text{H}_8$
 B_2H_6
 B_2H_6
 Formation: 5.3.2.5.1
 Reaction with alkynes: 5.3.2.5.1
 $\text{B}_2\text{I}_2^*\text{C}_{12}\text{H}_8$
 $\text{B}_2\text{I}_2\text{S}^*\text{C}_6\text{H}_{10}$
 $\text{B}_2\text{I}_4\text{MnO}_3^*\text{C}_8\text{H}_3$
 B_2Mg
 MgB_2
 Formation: 5.3.2.1.1
 $\text{B}_2\text{N}_2^*\text{C}_{16}\text{H}_{38}$
 $\text{B}_2\text{N}_2^*\text{C}_{16}\text{H}_{42}$
 $\text{B}_2\text{N}_2^*\text{C}_{18}\text{H}_{42}$
 $\text{B}_2\text{N}_2^*\text{C}_{20}\text{H}_{42}$
 $\text{B}_2\text{N}_2^*\text{C}_{20}\text{H}_{46}$
 $\text{B}_2\text{N}_2^*\text{C}_{26}\text{H}_{54}$
 $\text{B}_2\text{N}_2\text{Sn}_2^*\text{C}_{10}\text{H}_{30}$



Reaction with Cl_2 and elemental carbon: 5.3.2.2.2

Reaction with CO: 5.3.2.1.1

Reaction with elemental Si: 5.3.7.1

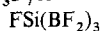
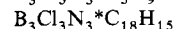
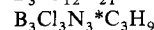
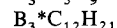
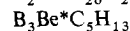
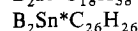
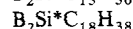
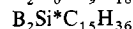
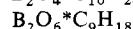
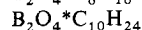
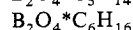
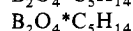
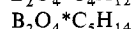
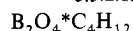
Reaction with elemental carbon:

5.3.2.1.1

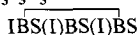
Reaction with graphite: 5.3.2.2.5

Reaction with magnesium metal:

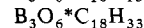
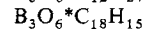
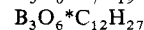
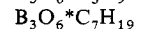
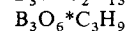
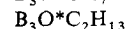
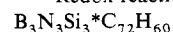
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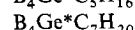
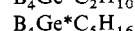
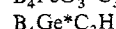
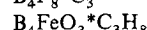
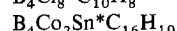
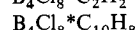
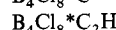
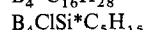
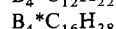
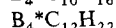
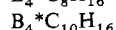
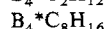
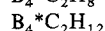
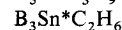
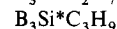
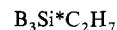
Formation: 5.3.7.2



Redox reaction: 5.3.2.3.4



Formation: 5.3.7.1

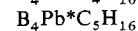
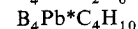
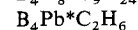
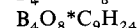
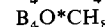
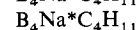
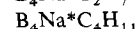
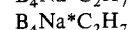
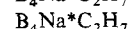
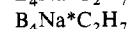
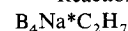


Reaction with $(CH_3)_2Hg$: 5.3.2.7.6

Reaction with CO: 5.3.2.7.5

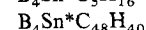
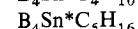
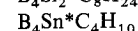
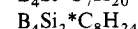
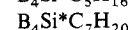
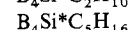
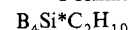
Reaction with alkynes: 5.3.2.7.3

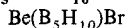
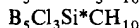
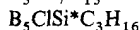
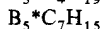
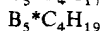
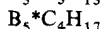
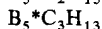
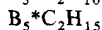
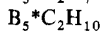
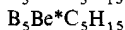
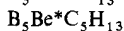
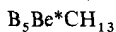
Reaction with ethylene: 5.3.2.7.6



Decomposition: 5.3.7.1

Formation: 5.3.7.1



B₅BeBrH₁₀Reaction with Na[C₅H₅]: 5.4.3.3.1Reaction with R₂GeX₂ and R₃GeX:

5.3.12.3

Reaction with R₃PbCl: 5.3.22.3.2Reaction with R₃SnX: 5.3.17.3.2Reaction with SiX₄: 5.3.7.3.2

Alkylation: 5.3.2.7.2

Hydroboration reagent: 5.3.2.7.1

Reaction with C₂H₅CH=CH₂: 5.3.2.7.1Reaction with Li[C≡CCH₃]: 5.3.2.7.4

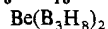
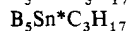
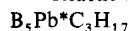
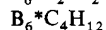
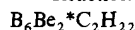
Reaction with NaCN: 5.3.2.7.4



Reaction with acetylene: 5.3.2.7.3



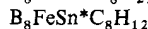
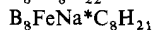
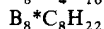
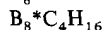
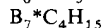
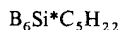
Reaction with CO: 5.3.2.7.5

Reaction with CH₂=CH₂: 5.3.2.7.1Reaction with Na[C₅H₅]: 5.4.3.3.1

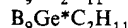
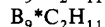
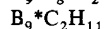
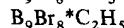
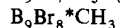
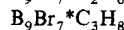
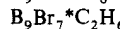
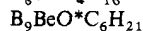
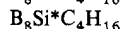
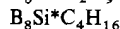
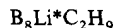
Reaction with alkynes: 5.3.2.7.3



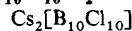
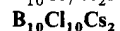
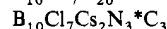
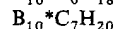
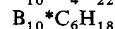
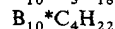
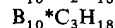
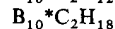
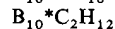
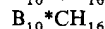
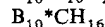
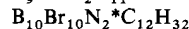
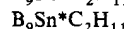
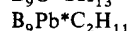
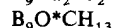
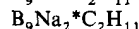
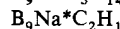
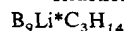
Formation: 5.3.7.1



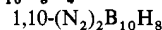
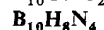
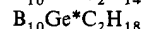
Reaction with alkynes: 5.3.2.7.3



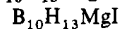
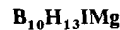
Reaction with CO: 5.3.2.7.5



Reaction with KCN: 5.3.2.7.4



Reaction with CO: 5.3.2.7.5

Reaction with [(C₂H₅)₃O][BF₄]:

5.3.2.7.6

- Reaction with $(\text{CH}_3)_2\text{SO}_4$: 5.3.2.7.6
 Reaction with alkyl halides: 5.3.2.7.6
- B₁₀H₁₃Na**
 $\text{Na}[\text{B}_{10}\text{H}_{13}]$
 Reaction with R_3GeX : 5.3.12.3
- B₁₀H₁₄**
 $\text{B}_{10}\text{H}_{14}$
 Alkylation: 5.3.2.7.2
 Reaction with KCN: 5.3.2.7.4
 Reaction with alkyl isocyanides: 5.3.2.7.4
- $\text{B}_{10}\text{NNA}_2 \cdot \text{CH}_{13}$
 $\text{B}_{10}\text{NO} \cdot \text{C}_4\text{H}_{17}$
 $\text{B}_{10}\text{N}_2 \cdot \text{C}_4\text{H}_{18}$
 $\text{B}_{10}\text{N}_2 \cdot \text{C}_6\text{H}_{22}$
 $\text{B}_{10}\text{Na} \cdot \text{CH}_{11}$
 $\text{B}_{10}\text{O} \cdot \text{C}_4\text{H}_{14}$
 $\text{B}_{10}\text{OS} \cdot \text{C}_3\text{H}_{14}$
 $\text{B}_{10}\text{O}_2 \cdot \text{C}_2\text{H}_8$
 $\text{B}_{10}\text{O}_2 \cdot \text{C}_8\text{H}_{18}$
 $\text{B}_{10}\text{O}_2 \cdot \text{C}_{14}\text{H}_{28}$
 $\text{B}_{10}\text{S} \cdot \text{C}_2\text{H}_{18}$
 $\text{B}_{10}\text{S} \cdot \text{C}_8\text{H}_{28}$
 $\text{B}_{10}\text{S}_2 \cdot \text{C}_4\text{H}_{24}$
 $\text{B}_{10}\text{S}_2 \cdot \text{C}_8\text{H}_{32}$
 $\text{B}_{10}\text{Si} \cdot \text{CH}_{20}$
 $\text{B}_{10}\text{Si} \cdot \text{C}_3\text{H}_{22}$
 $\text{B}_{10}\text{Sn} \cdot \text{C}_2\text{H}_{18}$
 $\text{B}_{10}\text{Sn} \cdot \text{C}_{12}\text{H}_{23}$
 $\text{B}_{12} \cdot \text{As}_2$
 $\text{B}_{12}\text{H}_{18}\text{O}_2$
 $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$
 Reaction with CO: 5.3.2.7.5
- B₁₂O₂**
 B_{12}O_2
 Formation: 5.3.2.1
- $\text{B}_{12}\text{O}_2 \cdot \text{C}_2\text{H}_{10}$
- B₁₂P₂**
 B_{12}P_2
 Formation: 5.3.2.1
- B₁₂S**
 B_{12}S
 Formation: 5.3.2.1
- B₁₆Si**
 B_{16}Si
 Formation: 5.3.7.1
- $\text{B}_{17}\text{Li} \cdot \text{C}_4\text{H}_{20}$
- B₁₈H₂₂**
 $i\text{-B}_{18}\text{H}_{22}$
 Reaction with cyclohexylisocyanide:
 5.3.2.7.4
- $\text{B}_{18}\text{N} \cdot \text{C}_7\text{H}_{33}$
 $\text{B}_{20}\text{Hg} \cdot \text{C}_4\text{H}_{22}$
- B₅₀Si**
 B_{50}Si
 Formation: 5.3.7.1
- Ba**
 Ba
 Reaction with PbR_4 : 5.4.7.2.3
 Reaction with Pb metal: 5.4.7.1.1
 Reaction with R_2Hg , R_2Cd , R_2Zn :
 5.4.3.2.2
 Reaction with R_6Ge_2 : 5.4.5.6
 Reaction with R_6Si_2 : 5.4.4.6
 Reaction with Sn metal: 5.4.6.1
 Reaction with RX: 5.4.3.2.1
- $\text{Ba} \cdot \text{C}_2\text{H}_6$
 $\text{Ba} \cdot \text{C}_8\text{H}_{20}\text{B}$
 $\text{Ba} \cdot \text{C}_{12}\text{H}_{10}$
 $\text{Ba} \cdot \text{C}_{12}\text{H}_{32}\text{Al}_2$
 $\text{Ba} \cdot \text{C}_{14}\text{H}_{14}$
 $\text{Ba} \cdot \text{C}_{16}\text{H}_{40}\text{Al}_2$
 $\text{Ba} \cdot \text{C}_{26}\text{H}_{18}$
 $\text{Ba} \cdot \text{C}_{28}\text{H}_{24}$
 $\text{Ba} \cdot \text{C}_{38}\text{H}_{30}$
 $\text{Ba} \cdot \text{C}_{42}\text{H}_{38}$
 $\text{BaCl} \cdot \text{C}_{19}\text{H}_{15}$
 $\text{BaGe}_2 \cdot \text{C}_{36}\text{H}_{30}$
 $\text{BaGe}_2\text{O} \cdot \text{C}_{40}\text{H}_{38}$
- BaH₂**
 BaH_2
 Reaction with AlEt_3 : 5.4.3.3.1
 Reaction with C_5H_6 : 5.4.3.4.2
 Reaction with olefins: 5.4.3.4.3
- $\text{BaHg} \cdot \text{C}_6\text{H}_4$
 $\text{BaHg} \cdot \text{C}_{32}\text{H}_{20}$
 $\text{BaIO} \cdot \text{C}_6\text{H}_{13}$
 $\text{BaN} \cdot \text{C}_{16}\text{H}_{16}$
 $\text{BaO}_2 \cdot \text{C}_4\text{H}_{10}$
- BaPb**
 BaPb
 Formation: 5.4.7.1.1
- BaPb₃**
 BaPb_3
 Formation: 5.4.7.1.1
- BaPdSn₃**
 BaPdSn_3
 Formation: 5.4.6.1
- $\text{BaSi}_2 \cdot \text{C}_{36}\text{H}_{30}$
- BaSn**
 BaSn
 Formation: 5.4.6.1
- BaSn₅**
 BaSn_5
 Formation: 5.4.6.1

- BaZn***C₈H₂₀
BaZn*C₈H₂₀
Ba₂Pb
 Ba₂Pb
 Formation: 5.4.7.1.1
Ba₂Sn
 Ba₂Sn
 Formation: 5.4.6.1
Ba₃Pb₅
 Ba₃Pb₅
 Formation: 5.4.7.1.1
Ba₅Pb₃
 Ba₅Pb₃
 Formation: 5.4.7.1.1
Ba₅Sn₃
 Ba₅Sn₃
 Formation: 5.4.6.1
Be
 Be
 Reaction with R₂Hg: 5.4.3.2.2
 Reaction with Sn metal: 5.4.6.1
 Reaction with RX: 5.4.3.2.1
BeBr*C₅H₅
BeBr*C₅H₁₁
BeBrH₁₀*B₅
BeBrN₂*C₈H₂₁
BeBrN₂*C₁₁H₂₇
BeBrO₂*C₅H₁₁
BeBrO₂*C₈H₁₉
BeBr₂
 BeBr₂
 Reaction with BeR₂ and LiH: 5.4.3.3.2
 Reaction with RMgX: 5.4.3.3.1
 Redistribution with BeR₂: 5.4.3.3.2
Be*CH₄
Be*CH₁₃B₅
Be*C₂D₆
Be*C₂H₆
Be*C₂H₆
Be*C₂H₆
Be*C₂H₆
Be*C₂H₆
Be*C₂H₆
Be*C₂H₆
Be*C₄H₁₀
Be*C₄H₁₀
Be*C₄H₁₀
Be*C₄H₁₀
Be*C₅H₁₂
Be*C₅H₁₃B₃
Be*C₅H₁₃B₅
Be*C₅H₁₅B₅
Be*C₆H₆
Be*C₆H₆
Be*C₆H₆
Be*C₆H₈
Be*C₆H₁₀
Be*C₆H₁₄
Be*C₇H₈
Be*C₇H₁₀
Be*C₈H₁₈
Be*C₈H₂₄Al₂
Be*C₉H₁₄
Be*C₁₀H₁₀
Be*C₁₀H₁₀
Be*C₁₀H₂₂
Be*C₁₁H₁₀
Be*C₁₂H₁₀
Be*C₁₂H₁₀
Be*C₁₂H₁₀
Be*C₁₄H₁₄
Be*C₁₄H₁₈
Be*C₁₆H₁₀
Be*C₁₆H₁₈
Be*C₁₆H₂₂
Be*C₁₆H₂₄Al₂
Be*C₁₈H₂₂
Be*C₂₀H₁₄
Be*C₂H₅
BeCl*C₄H₉
BeCl*C₅H₅
BeClN*C₁₁H₂₂
BeClN*C₁₂H₁₁
BeClO₂*C₅H₁₁
BeClO₂*C₈H₁₉
BeClO₂*C₁₀H₁₃
BeCl₂
 BeCl₂
 Reaction with RMgX: 5.4.3.3.1
 Reaction with BeR₂ and LiH: 5.4.3.3.2
 Reaction with Na[C₅H₅]: 5.4.3.3.1
 Reaction with C₁₄H₁₀: 5.4.3.3.1
 Redistribution with BeR₂: 5.4.3.3.2
BeCl₂*C₁₂H₈
BeF₅*C₁₁H₅
BeH₂
 BeH₂
 Reaction with olefins: 5.4.3.4.3
 Redistribution with BeR₂: 5.4.3.4.3
BeH₈*B₂
BeH₁₆*B₆
BeLi*C₅H₅
BeLi*C₃H₉
BeLi*C₁₈H₁₅

$\text{BeLi}^*\text{C}_{21}\text{H}_{21}$
 $\text{BeLiN}^*\text{C}_6\text{H}_{15}$
 $\text{BeLi}_2^*\text{C}_4\text{H}_{12}$
 $\text{BeLi}_2^*\text{C}_{32}\text{H}_{20}$
 $\text{BeLi}_3^*\text{C}_5\text{H}_{15}$
 $\text{BeN}^*\text{C}_5\text{H}_{15}$
 $\text{BeN}^*\text{C}_7\text{H}_{11}$
 $\text{BeN}^*\text{C}_9\text{H}_{15}$
 $\text{BeN}^*\text{C}_9\text{H}_{23}$
 $\text{BeN}^*\text{C}_{13}\text{H}_{31}$
 $\text{BeN}^*\text{C}_{13}\text{H}_{31}$
 $\text{BeN}_2^*\text{C}_4\text{H}_{12}$
 $\text{BeN}_2^*\text{C}_{10}\text{H}_{26}$
 $\text{BeN}_2^*\text{C}_{12}\text{H}_{30}$
 $\text{BeN}_2\text{O}^*\text{C}_{12}\text{H}_{16}$
 $\text{BeN}_2\text{O}^*\text{C}_{15}\text{H}_{22}$
 $\text{BeNa}^*\text{C}_4\text{H}_{11}$
 $\text{BeNa}^*\text{C}_{31}\text{H}_{25}$
 $\text{BeO}^*\text{C}_6\text{H}_{21}\text{B}_9$
 $\text{BeO}^*\text{C}_{12}\text{H}_{28}$
 $\text{BeO}^*\text{C}_{20}\text{H}_{20}$
 $\text{BeO}_2^*\text{C}_4\text{H}_{10}$
 $\text{BeO}_2^*\text{C}_8\text{H}_{18}$
 $\text{BeO}_2^*\text{C}_9\text{H}_{24}$
 $\text{BeO}_2^*\text{C}_{10}\text{H}_{26}$
 $\text{BeO}_2^*\text{C}_{12}\text{H}_{30}$
 $\text{BeO}_2^*\text{C}_{14}\text{H}_{26}$
 $\text{BeO}_2^*\text{C}_{16}\text{H}_{30}$
 $\text{BeO}_2^*\text{C}_{24}\text{H}_{26}$
 $\text{BeO}_2\text{P}_4^*\text{C}_{10}\text{H}_{32}\text{B}_2$
 $\text{BeP}_4^*\text{C}_{12}\text{H}_{36}\text{B}_2$
 $\text{BeS}_2^*\text{C}_4\text{H}_{10}$
 $\text{BeS}_2^*\text{C}_8\text{H}_{18}$
 $\text{BeSi}_2^*\text{C}_8\text{H}_{22}$
 $\text{Be}_2^*\text{C}_2\text{H}_{14}\text{B}_2$
 $\text{Be}_2^*\text{C}_2\text{H}_{22}\text{B}_6$
 $\text{Be}_2^*\text{C}_6\text{H}_{16}$
 $\text{Be}_2^*\text{C}_{12}\text{H}_{28}$
 $\text{Be}_2^*\text{C}_{22}\text{H}_{32}$
 $\text{Be}_2^*\text{C}_{24}\text{H}_{18}$
 $\text{Be}_2\text{FK}^*\text{C}_8\text{H}_{20}$
 $\text{Be}_2\text{K}_2\text{O}_2^*\text{C}_{16}\text{H}_{38}$
 $\text{Be}_2\text{Li}^*\text{C}_5\text{H}_{15}$
 $\text{Be}_2\text{Li}_2\text{O}_4^*\text{C}_{20}\text{H}_{46}$
 $\text{Be}_2\text{N}_2^*\text{C}_6\text{H}_{20}$
 $\text{Be}_2\text{N}_2^*\text{C}_8\text{H}_{24}$
 $\text{Be}_2\text{N}_2^*\text{C}_8\text{H}_{26}$
 $\text{Be}_2\text{N}_2^*\text{C}_{14}\text{H}_{30}$
 $\text{Be}_2\text{N}_2^*\text{C}_{16}\text{H}_{42}$
 $\text{Be}_2\text{N}_2^*\text{C}_{18}\text{H}_{30}$
 $\text{Be}_2\text{N}_2^*\text{C}_{20}\text{H}_{42}$
 $\text{Be}_2\text{N}_2^*\text{C}_{30}\text{H}_{54}$

$\text{Be}_3^*\text{C}_{15}\text{H}_{36}$
 $\text{Be}_3\text{N}_3^*\text{C}_9\text{H}_{27}$
 $\text{Be}_3\text{O}_6^*\text{C}_{24}\text{H}_{54}$
 $\text{Be}_4\text{O}_4^*\text{C}_8\text{H}_{24}$
 $\text{Be}_4\text{O}_4^*\text{C}_{20}\text{H}_{48}$
 $\text{Be}_4\text{S}_4^*\text{C}_{16}\text{H}_{40}$
 $\text{Br}^*\text{C}_2\text{H}_5$
 $\text{Br}^*\text{C}_2\text{H}_5\text{B}$
 $\text{Br}^*\text{C}_4\text{H}_{10}\text{Al}$
 $\text{Br}^*\text{C}_4\text{H}_{10}\text{B}$
 $\text{Br}^*\text{C}_5\text{H}_5\text{Be}$
 $\text{Br}^*\text{C}_5\text{H}_{11}\text{Be}$
 $\text{Br}^*\text{C}_7\text{H}_8\text{B}$
 $\text{Br}^*\text{C}_8\text{H}_{18}\text{B}$
 $\text{Br}^*\text{C}_{12}\text{H}_{10}\text{B}$
 $\text{Br}^*\text{C}_{15}\text{H}_{15}$
 $\text{BrCl}_3\text{In}_2^*\text{CH}_2$
 $\text{BrF}_2\text{In}^*\text{C}_{12}\text{H}_8$
 $\text{BrF}_4^*\text{C}_{12}\text{H}_{10}\text{B}$
 $\text{BrF}_5\text{Mg}^*\text{C}_6$
 $\text{BrF}_{10}\text{In}^*\text{C}_{12}$
 $\text{BrF}_{10}\text{Tl}^*\text{C}_{12}$
 $\text{BrF}_{15}\text{MgPb}^*\text{C}_{18}$
 $\text{BrGa}^*\text{C}_8\text{H}_{18}$
 $\text{BrGa}^*\text{C}_{12}\text{H}_{10}$
 $\text{BrGaGe}_2^*\text{C}_{12}\text{H}_{30}$
 $\text{BrGaSi}_2^*\text{C}_8\text{H}_{22}$
 $\text{BrGe}^*\text{C}_3\text{H}_9$
 $\text{BrGeMg}^*\text{C}_{18}\text{H}_{15}$
 $\text{BrGeMg}^*\text{C}_{18}\text{H}_{15}$
BrHMg

HMgBr

Addition to alkynes: 5.4.2.4.1

Addition to olefins: 5.4.2.4.1

$\text{BrH}_{10}^*\text{B}_5\text{Be}$

BrIn

InBr

Reaction with RHgX : 5.3.5.3.4

Reaction with RI: 5.3.5.3.3

Reaction with R_2Hg : 5.3.5.3.4

$\text{BrIn}^*\text{C}_2\text{H}_6$

$\text{BrIn}^*\text{C}_{12}\text{H}_{10}$

$\text{BrIn}^*\text{C}_{14}\text{H}_{14}$

$\text{BrIn}^*\text{C}_{20}\text{H}_{14}$

$\text{BrIn}^*\text{C}_{27}\text{H}_{21}$

$\text{BrInO}_4^*\text{C}_8\text{H}_{14}$

BrMg^*CH_3

BrMg^*CH_3

BrMg^*CH_3

BrMg^*CH_3

$\text{BrMg}^*\text{C}_2\text{H}$

$\text{BrMg}^*\text{C}_2\text{H}_3$

- BrMg*C₂H₅
 BrMg*C₂H₅
 BrMg*C₃H₃
 BrMg*C₃H₅
 BrMg*C₃H₅
 BrMg*C₃H₇
 BrMg*C₄H₉
 BrMg*C₄H₉
 BrMg*C₅H₅
 BrMg*C₅H₇
 BrMg*C₅H₁₁
 BrMg*C₆H₅
 BrMg*C₆H₅
 BrMg*C₆H₉
 BrMg*C₆H₉
 BrMg*C₆H₁₁
 BrMg*C₇H₇
 BrMg*C₈H₇
 BrMg*C₈H₉
 BrMg*C₉H₇
 BrMg*C₉H₉
 BrMg*C₉H₁₁
 BrMg*C₉H₁₇
 BrMg*C₁₀H₇
 BrMg*C₁₁H₉
 BrMg*C₁₃H₁₁
 BrMg*C₁₃H₁₅
 BrMg*C₁₄H₉
 BrMg*C₁₆H₁₅
 BrMg*C₁₉H₁₃
 BrMg*C₁₉H₁₅
 BrMg*C₁₉H₁₅
 BrMgN*C₅H₄
 BrMgN*C₈H₁₀
 BrMgN*C₉H₂₀
 BrMgNO*C₁₂H₁₂
 BrMgNSn*C₂₄H₃₀
 BrMgN₂*C₇H₁₉
 BrMgO*C₉H₁₄
 BrMgOSi*C₁₄H₂₉
 BrMgO₂S*C₉H₉
 BrMgO₂S*C₁₄H₁₁
 BrMgPb*C₁₈H₁₅
 BrMgPb*C₁₈H₁₅
 BrMgS*C₄H₃
 BrMgSi*C₅H₁₁
 BrMgSi*C₁₇H₁₅
 BrMgSi*C₁₇H₂₂
 BrMgSi*C₁₈H₁₅
 BrMgSi*C₁₈H₁₅
 BrMgSn*C₃H₉
 BrMgSn*C₁₆H₁₅
 BrMgSn*C₁₈H₁₅
 BrMgSn*C₁₈H₁₉
 BrN₂*C₈H₂₁Be
 BrN₂*C₁₁H₂₇Be
 BrO₂*C₅H₁₁Be
 BrO₂*C₈H₁₉Be
 BrPb*C₆H₁₅
 BrS*C₂H₈B
 BrSi*C₁₁H₁₃
 BrSn*C₃H₉
 BrTi
 TlBr
 Reaction with RMgX: 5.3.6.3.1
 Reaction with X₂: 5.3.6.3.1
Br₂
 Br₂
 Reaction with TlBr: 5.3.6.3.1
 Br₂*Be
 Br₂*Be
 Br₂*Be
 Br₂*CH₃B
 Br₂*C₂H₃B
 Br₂*C₂H₅B
 Br₂*C₆H₅B
 Br₂*C₁₃H₁₁B
 Br₂ClS*C₇H₁₄B
 Br₂FIn*C₆H₄
 Br₂Fe*C₁₀H₉B
 Br₂FeMg₂*C₁₀H₈
Br₂Ga
 GaBr₂
 Reaction with RX: 5.3.4.3.3
 Br₂Ga*C₆H₅
Br₂GaH
 Br₂GaH
 Reaction with olefins: 5.3.4.4.1
 Br₂GaSi*C₄H₁₁
Br₂Hg
 HgBr₂
 Reaction with In metal and HgPh₂:
 5.3.5.2.5
 Br₂Hg₂*C₃H₆
Br₂In
 InBr₂
 Reaction with RI: 5.3.5.3.3
 Br₂In*CH₃
 Br₂In*C₅H₅
 Br₂In*C₃H₇
 Br₂In*C₄H₉
 Br₂In*C₆H₅
 Br₂In*C₇H₇
 Br₂InN₂*C₈H₂₁
Br₂Mg
 MgBr₂
 Formation: 5.4.2.3.1

- Reaction with RLi: 5.4.2.3.1
 Reaction with RNa: 5.4.2.3.1
 Reaction with radicals: 5.4.2.3.3
 Redistribution with MgR_2 : 5.4.2.3.2
- $\text{Br}_2\text{Mg}_2\text{C}_2$
 $\text{Br}_2\text{Mg}_2\text{C}_3\text{H}_4$
 $\text{Br}_2\text{Mg}_2\text{C}_3\text{H}_6$
 $\text{Br}_2\text{Mg}_2\text{C}_3\text{H}_6$
 $\text{Br}_2\text{Mg}_2\text{C}_5\text{H}_{10}$
 $\text{Br}_2\text{Mg}_2\text{C}_6\text{H}_4$
 $\text{Br}_2\text{Mg}_2\text{O}\text{C}_6\text{H}_{12}$
 $\text{Br}_2\text{Mg}_2\text{O}\text{C}_7\text{H}_{12}$
 $\text{Br}_2\text{Mg}_2\text{Sn}_2\text{C}_{36}\text{H}_{30}$
 $\text{Br}_2\text{MnO}_3\text{C}_8\text{H}_4\text{B}$
 $\text{Br}_2\text{MnO}_3\text{C}_9\text{H}_6\text{B}$
 $\text{Br}_2\text{P}_6\text{Sn}\text{C}_{81}\text{H}_{81}\text{B}$
 $\text{Br}_2\text{P}_8\text{Sn}\text{C}_{105}\text{H}_{99}\text{B}_2$
- Br_2Pb**
 PbBr_2
 Reaction with $\text{Na}[\text{C}_2\text{B}_4\text{H}_7]$: 5.3.22.3.2
 Reaction with $\text{Na}[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]$:
 5.3.22.3.2
 Reaction with RMgX : 5.4.7.2.5
- $\text{Br}_2\text{S}\text{C}_2\text{H}_7\text{B}$
 $\text{Br}_2\text{S}\text{C}_8\text{H}_{17}\text{B}$
 $\text{Br}_2\text{S}\text{C}_8\text{H}_{19}\text{B}$
 Br_3Al
 Br_3B
 Br_3B
 Br_3B
 Br_3B
 $\text{Br}_3\text{C}_3\text{H}_9\text{Al}_2$
 $\text{Br}_3\text{C}_6\text{H}_{15}\text{Al}_2$
 $\text{Br}_3\text{C}_8\text{H}_6\text{B}$
 $\text{Br}_3\text{C}_9\text{H}_{15}\text{Al}_2$
 $\text{Br}_3\text{C}_{18}\text{H}_{15}\text{Al}_2$
- Br_3Ga**
 GaBr_3
 Reaction with RMgX : 5.3.4.3.1
 Reaction with R_3Al : 5.3.4.3.1
 Reaction with R_3Ga : 5.3.4.3.5
 Reaction with SiR_4 : 5.3.4.3.1
- $\text{Br}_3\text{Ga}\text{C}_{18}\text{H}_{12}$
 $\text{Br}_3\text{Ga}_2\text{C}_3\text{H}_9$
 $\text{Br}_3\text{Ga}_2\text{C}_6\text{H}_{15}$
- Br_3In**
 InBr_3
 Reaction with InR_3 : 5.3.5.3.2
- $\text{Br}_3\text{In}\text{C}_{18}\text{H}_{12}$
 $\text{Br}_3\text{In}_2\text{C}_3\text{H}_9$
 $\text{Br}_3\text{In}_2\text{C}_6\text{H}_{15}$
 $\text{Br}_3\text{In}_2\text{C}_9\text{H}_{21}$
 $\text{Br}_3\text{In}_2\text{C}_{12}\text{H}_{27}$
- Br_3Ti**
 TiBr_3
 Formation: 5.3.6.3.1
 Reaction with RB(OH)_2 : 5.3.6.3.3
- Br_4B_2
 $\text{Br}_4\text{C}_5\text{H}_4\text{B}_2$
 $\text{Br}_4\text{CoP}_4\text{C}_{52}\text{H}_{48}\text{B}_2$
 $\text{Br}_4\text{Fe}\text{C}_{10}\text{H}_8\text{B}_2$
- Br_4Ga_2**
 Ga_2Br_4
 Reaction with RX : 5.3.4.3.3
- $\text{Br}_7\text{C}_2\text{H}_6\text{B}_9$
 $\text{Br}_7\text{C}_3\text{H}_8\text{B}_9$
 $\text{Br}_8\text{CH}_3\text{B}_9$
 $\text{Br}_8\text{C}_2\text{H}_5\text{B}_9$
 $\text{Br}_{10}\text{N}_2\text{C}_{12}\text{H}_{32}\text{B}_{10}$
- C**
C
 Reaction with BX_3 , B_2X_4 : 5.3.2.3.4
 Reaction with B_2O_3 : 5.3.2.1.1
 Reaction with elemental boron: 5.3.2.1.1,
 5.3.2.2.1
- CB_4**
 B_4C
 Crystal growth: 5.3.2.2.6, 5.3.2.2.7
 Formation: 5.3.2.1, 5.3.2.1.1, 5.3.2.2.1,
 5.3.2.2.2, 5.3.2.2.3, 5.3.2.2.5, 5.3.2.2.6
 Hot pressing: 5.3.2.1.2
 Reaction with elemental boron: 5.3.2.2.1
 Sintering: 5.3.2.1.2
- CB_3Cl_8**
 $\text{C}(\text{BCl}_2)_4$
 Formation: 5.3.2.3.4
- CB_8**
 B_8C
 Formation: 5.3.2.2.3
- CCl_4**
 CCl_4
 Reaction with $\text{Li}/(\text{MeO})_2\text{BCl}$: 5.3.2.3.2
- CCl_4Mg**
 Cl_3CMgCl
 Formation: 5.4.2.5.2
- CD_3IMg**
 CD_3MgI
 Reaction with BeCl_2 : 5.4.3.3.1
- CHCl_3**
 CHCl_3
 Reaction with $\text{Li}/(\text{MeO})_2\text{BCl}$: 5.3.2.3.2
 Reaction with RMgX : 5.4.2.5.2
- CHN**
HCN
 Reaction with R_2AlH : 5.3.3.5.2

- CH₂Al₂Cl₄**
 CH₂(AlCl₂)₂
 Formation: 5.3.3.2.2
- CH₂BF₃**
 FCH₂BF₂
 Formation: 5.3.2.3.5
- CH₂BrCl₃In₂**
 ClBrInCH₂InCl₂
 Formation: 5.3.5.3.3
- CH₂Cl₂**
 CH₂Cl₂
 Reaction with Al metal: 5.3.3.2.2
 Reaction with Li/(MeO)₂BCl: 5.3.2.3.2
- CH₂Cl₃IIn₂**
 IClInCH₂InCl₂
 Formation: 5.3.5.3.3
- CH₂Cl₄In₂**
 Cl₂InCH₂InCl₂
 Formation: 5.3.5.3.3
- CH₂Cl₄Si**
 Cl₃SiCH₂Cl
 Reaction with B₃H₉: 5.3.2.7.2
- CH₂I₂Mg₂**
 CH₂(MgI)₂
 Formation: 5.4.2.2.1
- CH₂N₂**
 CH₂N₂
 Polymerization with BX₃: 5.3.2.3.5
 Reaction with BX₃: 5.3.2.3.5
 Reaction with RTiCl₂, TiCl₃: 5.3.6.3.6
 Reaction with R₂GaX: 5.3.4.3.4
 Reaction with R₃Al: 5.3.3.5.5
- CH₃AlCl₂**
 CH₃AlCl₂
 Reaction with BX₃: 5.3.2.3.1
- CH₃AlCl₃Na**
 Na[CH₃AlCl₃]
 Formation: 5.3.3.2.2
- CH₃B**
 CH₃B
 Addition to alkynes: 5.3.2.3.2
 Addition to olefins: 5.3.2.3.2
 Formation: 5.3.2.3.2
 Insertion into C—H bonds: 5.3.2.3.2
- CH₃BBr₂**
 CH₃BBr₂
 Formation: 5.3.2.3.1
 Reaction with M—C bonds: 5.3.2.3.1
- CH₃BCl₂**
 CH₃BCl₂
 Formation: 5.3.2.3.1
- CH₃BCl₂O₂**
 Cl₂CHB(OH)₂
 Formation: 5.3.2.4.1
- CH₃BF₂**
 CH₃BF₂
 Formation: 5.3.2.3.1
- CH₃BI₂**
 CH₃BI₂
 Formation: 5.3.2.3.1
 Reaction with h⁵-C₅H₅—M bonds: 5.3.2.3.3
- CH₃BO**
 OCBH₃
 Formation: 5.3.2.7.5
- CH₃B₉Br₈**
 CH₃B₉Br₈
 Formation: 5.3.2.7.6
- CH₃BrMg**
 CH₃MgBr
 Formation: 5.4.2.2.1, 5.4.2.3.1
- CH₃BrMg**
 CH₃MgBr
 Reaction with (CO)₄CoGePh₃: 5.4.5.4
 Reaction with (CO)₄CoSiMePh(1-Np): 5.4.4.5
 Reaction with (CO)₄CoSiPh₃: 5.4.4.5
 Reaction with R₆Sn₂: 5.4.6.4
- CH₃Br₂In**
 CH₃InBr₂
 Formation: 5.3.5.3.3
- CH₃CaI**
 CH₃CaI
 Addition to olefins: 5.4.3.4.1
 Formation: 5.4.3.2.1
 Half-life in Ether: 5.4.3.2.1
 Metallation of RH: 5.4.3.4.2
- CH₃Cl**
 CH₃Cl
 Reaction with Al metal: 5.3.3.2.2
- CH₃ClMg**
 CH₃MgCl
 Reaction with PbX₂: 5.4.7.2.5
- CH₃Cl₂Ga**
 CH₃GaCl₂
 Formation: 5.3.4.3.1, 5.3.4.3.2
- CH₃Cl₂In**
 CH₃InCl₂
 Formation: 5.3.5.3.2
- CH₃Cl₃Ge**
 CH₃GeCl₃
 Reaction with Na₃[CHB₁₀H₁₀]: 5.3.12.3
- CH₃GaO**
 H₃CGaO
 Formation: 5.3.4.2.5
- CH₃IMg**
 CH₃MgI
 Formation: 5.4.2.2.1

- Reaction with R_3SiLi : 5.4.4.7
 Reaction with $BeCl_2$: 5.4.3.3.1
 Reaction with olefins: 5.4.2.5.1
 CH_3I_2In
 CH_3InI_2
 Formation: 5.3.5.3.2, 5.3.5.3.3
 Reaction with InX_3 : 5.3.5.3.2
 $CH_3I_5In_2$
 $I_2In \cdots I \cdots InI(CH_3)I$
 Formation: 5.3.5.3.2
 CH_3In
 CH_3In
 Reaction with InX : 5.3.5.3.3
 CH_3Li
 CH_3Li
 Reaction with $Li[AlH_4]$: 5.3.3.4.4
 Reaction with 2,3- $C_2B_9H_{11}$: 5.3.2.7.6
 Reaction with BeR_2 : 5.4.3.4.4
 Reaction with MgH_2 : 5.4.2.4.3
 Reaction with MgX_2 : 5.4.2.3.1
 CH_4
 CH_4
 Reaction with BCl_3 : 5.3.2.2.4
 CH_4Be
 CH_3BeH
 Formation: 5.4.3.3.2
 CH_4Cl_2Si
 $CH_3(H)SiCl_2$
 Reaction with $NaC_2B_4H_7$: 5.3.7.3.2
 CH_4Mg
 CH_3MgH
 Formation: 5.4.2.4.3
 CH_5LiMg
 $LiMgH_2CH_3$
 Formation: 5.4.2.4.3
 CH_6Mg_2
 $(CH_3)Mg_2H_3$
 Formation: 5.4.2.4.3
 CH_7B_3O
 OCB_3H_7
 Formation: 5.3.2.7.5
 CH_8B_2
 $CH_3HBH_2BH_2$
 Redistribution: 5.3.2.5.3
 CH_8B_4O
 OCB_4H_8
 Formation: 5.3.2.7.5
 CH_9B_5
 nido- CB_5H_9
 Formation: 5.3.2.7.3
 2- CB_5H_9
 Formation: 5.3.2.7.1
 $CH_{10}B_5Cl_3Si$
 $1-Cl_3SiCH_2B_5H_8$
 Formation: 5.3.2.7.2
 $CH_{11}B_5$
 $1-CH_3B_5H_8$
 Formation: 5.3.2.7.2
 $CH_{11}B_{10}Na$
 $Na[CHB_{10}H_{10}]$
 Reaction with $RGeX_3$: 5.3.12.3
 $CH_{12}B_4$
 $2-CH_3B_4H_9$
 Formation: 5.3.2.7.6
 $CH_{13}B_5Be$
 $CH_3BeB_5H_{10}$
 Formation: 5.4.3.3.1
 $CH_{13}B_9O$
 OCB_9H_{13}
 Formation: 5.3.2.7.5
 $CH_{13}B_{10}NNa_2$
 $Na_2[B_{10}H_{13}CN]$
 Formation: 5.3.2.7.4
 $CH_{16}B_{10}$
 $5-CH_3B_{10}H_{13}$
 Formation: 5.3.2.7.6
 $6-CH_3B_{10}H_{13}$
 Formation: 5.3.2.7.6
 $CH_{20}B_{10}Si$
 $2,2'-CH_3(H)Si(B_5H_8)_2$
 Formation: 5.3.7.3.2
 Cl_4
 Cl_4
 Reaction with BI_3 : 5.3.2.2.3
 CKN
 KCN
 Reaction with $Cs_2[B_{10}Cl_{10}]$: 5.3.2.7.4
 $CNNa$
 $NaCN$
 Reaction with B_5H_9 : 5.3.2.7.4
 CO
 CO
 Reaction with B_2O_3 : 5.3.2.1.1
 Reaction with $(CH_3)_2O \cdot B_3H_7$: 5.3.2.7.5
 Reaction with B_4H_{10} : 5.3.2.7.5
 Reaction with B_5H_{11} : 5.3.2.7.5
 Reaction with B_9H_{15} : 5.3.2.7.5
 Reaction with 1,10- $(N_2)_2B_{10}H_8$: 5.3.2.7.5
 CO_2
 CO_2
 Reaction with $R_3GeMgCl$: 5.4.5.3
 CSi
 SiC
 Reaction with BX_3 : 5.3.7.1

C₂B₂Cl₆
 (Cl₂B)ClC≡C(BCl₂)Cl
 Formation: 5.3.2.3.4

C₂Br₂Mg₂
 BrMgC≡CMgBr
 Formation: 5.4.2.5.2

C₂Ca
 CaC₂
 Reaction with Pb: 5.4.7.1.2
 Reaction with C₅H₆: 5.4.3.4.2

C₂D₆Be
 (CD₃)₂Be
 Formation: 5.4.3.3.1

C₂HBf₂
 HC≡CBF₂
 Formation: 5.3.2.3.1

C₂HBrMg
 HC≡CMgBr
 Formation: 5.4.2.5.2

C₂HNa
 Na[C≡CH]
 Reaction with AlCl₃: 5.3.3.3.1

C₂H₂
 HC≡CH
 Carbalumination: 5.3.3.5.1
 Hydroalumination: 5.3.3.4.1
 Reaction with B₂X₄: 5.3.2.3.4
 Reaction with B₂H₆: 5.3.2.5.1

C₂H₂BCl₃
 Cl₂BCH=CHCl
 Formation: 5.3.2.4

C₂H₂B₂Cl₄
 cis-C₂H₂(BCl₂)₂
 Formation: 5.3.2.3.4

C₂H₂B₂F₄
 cis-C₂H₂(BF₂)₂
 Formation: 5.3.2.3.4

C₂H₂B₄Cl₈
 cis-C₂H₂(BCl₂)₄
 Formation: 5.3.2.3.4

C₂H₂Cl₂Hg
 ClHgCH=CHCl
 Reaction with BX₃: 5.3.2.4

C₂H₃BBr₂
 CH₂=CHBBr₂
 Formation: 5.3.2.3.1

C₂H₃BCl₂
 CH₂=CHBCl₂
 Formation: 5.3.2.3.1
 Reaction with dienes: 5.3.2.6.4

C₂H₃BF₂
 CH₂=CHBF₂
 Formation: 5.3.2.3.1

C₂H₃BrMg
 CH₂=CHMgBr
 Reaction with B(OR)₃: 5.3.2.4.1

C₂H₃Cl₂Ga
 CH₂=CHGaCl₂
 Formation: 5.3.4.3.1

C₂H₃Cl₂Tl
 CH₂=CHTlCl₂
 Formation: 5.3.6.3.3

C₂H₄
 CH₂=CH₂
 Reaction with RBeH: 5.4.3.4.3
 Reaction with R₃Al: 5.3.3.5.1

C₂H₄BClN₂
 [(CH₂)₂N₂]BCl
 Reaction with Li[R₃Sn]: 5.3.17.2.2

C₂H₄BClO₂
 (HO)₂BCH=CHCl
 Formation: 5.3.2.4

C₂H₄Cl₃Tl
 (ClCH₂)₂TlCl
 Explosive solid: 5.3.6.3.6

C₂H₄Cl₄Ga₂
 Cl₂GaCH₂CH₂GaCl₂
 Formation: 5.3.4.4.1

C₂H₅AlCl₂
 C₂H₅AlCl₂
 Complex with KCl: 5.3.3.3.2
 Redistribution (base influence): 5.3.3.3.2

C₂H₅BBr₂
 C₂H₅BBr₂
 Formation: 5.3.2.3.1

C₂H₅BCl₂
 C₂H₅BCl₂
 Formation: 5.3.2.3.1
 Reaction with Li/THF: 5.3.2.3.2

C₂H₅BF₂
 C₂H₅BF₂
 Reaction with Li/THF: 5.3.2.3.2

C₂H₅BI₂
 C₂H₅BI₂
 Formation: 5.3.2.3.1

C₂H₅BO₂
 CH₃=CHB(OH)₂
 Reaction with TiX₃: 5.3.6.3.3

C₂H₅B₃
 closo-1,5-C₂B₃H₅
 Formation: 5.3.2.7.3
 Reaction with CH₃C≡CH: 5.3.2.7.1

C₂H₅B₉Br₈
 C₂H₅B₉Br₈
 Formation: 5.3.2.7.6

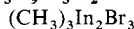
- C₂H₅BeCl**
 C₂H₅BeCl
 Formation: 5.4.3.3.1, 5.4.3.3.2
- C₂H₅Br**
 CH₃CH₂Br
 Initiator in the reaction of Mg with
 Ph₃SnCl: 5.4.6.2
- C₂H₅BrMg**
 C₂H₅MgBr
 Formation: 5.4.2.2.1
 Reaction with (CO)₄CoSiPh₃: 5.4.4.5
 Reaction with ArH: 5.4.2.5.2
 Reaction with BeCl₂: 5.4.3.3.1
 Reaction with alkynes: 5.4.2.5.2
 Solvent drying: 5.4.2.2.1
- C₂H₅Br₂In**
 C₂H₅InBr₂
 Formation: 5.3.5.3.3
- C₂H₅CaI**
 C₂H₅CaI
 Formation: 5.4.3.2.1
- C₂H₅Cl**
 C₂H₅Cl
 Reaction with Al metal: 5.3.3.2.2
- C₂H₅ClMg**
 C₂H₅MgCl
 Reaction with PbX₂: 5.4.7.2.5
- C₂H₅ClMgO**
 CH₃OCH₂MgCl
 Formation: 5.4.2.2.1
- C₂H₅Cl₂Ga**
 C₂H₅GaCl₂
 Formation: 5.3.4.4.1
- C₂H₅Cl₃Mg₂**
 C₂H₅Mg₂Cl₃
 Formation in THF: 5.4.2.3.2
- C₂H₅I₂In**
 C₂H₅InI₂
 Formation: 5.3.5.2.2, 5.3.5.3.3
- C₂H₅In**
 C₂H₅In
 Reaction with InX: 5.3.5.3.3
- C₂H₆AlCl**
 (CH₃)₂AlCl
 Reaction with NaF: 5.3.3.3.2
 Reaction with alkynes and Al metal:
 5.3.3.3.4
- C₂H₆AlF₂Na**
 Na[(CH₃)₂AlF₂]
 Decomposition: 5.3.3.3.2
- C₂H₆BBr**
 (CH₃)₂BBr
 Formation: 5.3.2.3.1
- C₂H₆BCl**
 (CH₃)₂BCl
 Formation: 5.3.2.3.1
- C₂H₆BClO₂**
 (CH₃O)₂BCl
 Reaction with Li/CH₂Cl₂: 5.3.2.3.2
 Reaction with Li/CHCl₃: 5.3.2.3.2
 Reaction with Li/CCl₄: 5.3.2.3.2
- C₂H₆BI**
 (CH₃)₂BI
 Formation: 5.3.2.3.1
- C₂H₆B₃Sn**
 SnC₂B₃H₆
 Formation: 5.3.17.3.2
- C₂H₆B₄**
 closo-1,6-C₂B₄H₆
 Formation: 5.3.2.7.3
 Hydroboration reagent: 5.3.2.7.1
- C₂H₆B₄Pb**
 closo-PbC₂B₄H₆
 Formation: 5.3.22.3.2
- C₂H₆B₉Br₇**
 (CH₃)₂B₉Br₇
 Formation: 5.3.2.7.6
- C₂H₆Ba**
 (CH₃)₂Ba
 Formation: 5.4.3.2.1
- C₂H₆Be**
 (CH₃)₂Be
 Formation: 5.4.3.2.2, 5.4.3.3.1, 5.4.3.3.1
 Reaction with Li[AlH₄]: 5.3.3.4.4
 Reaction with (AlR₃)₂: 5.4.3.4.4
 Reaction with R₃Ga: 5.3.4.5.2
 Reaction with [Be(OR)₂]₃: 5.4.3.3.2
 Reaction with LiR: 5.4.3.4.4
 Reaction with BR₃: 5.4.3.4.4
 Redistribution with BeX₂: 5.4.3.3.2
 Redistribution with BeR₂: 5.4.3.4.4
- C₂H₅BeH**
 Formation: 5.4.3.3.2
 Reaction with olefins: 5.4.3.4.3
- C₂H₆BrIn**
 (CH₃)₂InBr
 Reaction with Me₃P=CH₂: 5.3.5.4.2
- C₂H₆Ca**
 (CH₃)₂Ca
 Formation: 5.4.3.2.1
- C₂H₆Cd**
 (CH₃)₂Cd
 Reaction with Li[AlH₄]: 5.3.3.4.4
- C₂H₆ClGa**
 (CH₃)₂GaCl
 Reaction with R₃P=CH₂: 5.3.4.5.1

- C₂H₆ClIn**
 (CH₃)₂InCl
 Formation: 5.3.5.3.1
 Reaction with Me₃P=CH₂: 5.3.5.4.2
- C₂H₆Cl₂Si**
 (CH₃)₂SiCl₂
 Reaction with Mg metal and olefins: 5.4.2.2.4
- C₂H₆Cl₂Sn**
 (CH₃)₂SnCl₂
 Formation: 5.3.2.3.1
- C₂H₆Ga₂I₄**
 (CH₃)₂Ga₂I₄
 Formation: 5.3.4.2.1
- C₂H₆Hg**
 (CH₃)₂Hg
 Formation: 5.3.4.5.3
 Reaction with Al metal: 5.3.3.2.3
 Reaction with B₄H₁₀: 5.3.2.7.6
 Reaction with Ga metal: 5.3.4.2.3
 Reaction with Be metal: 5.4.3.2.2
- C₂H₆IIIn**
 (CH₃)₂InI
 Formation: 5.3.5.2.2, 5.3.5.2.8, 5.3.5.3.1
 Reaction with InX₃: 5.3.5.3.2
 Reaction with RInX₂: 5.3.5.3.2
- C₂H₆ITI**
 (CH₃)₂TII
 Formation: 5.3.6.2.9
- C₂H₆Mg**
 (CH₃)₂Mg
 Formation: 5.4.2.4.3
 Reaction with R₃Al: 5.3.3.5.4
 Reaction with MgX₂: 5.4.2.3.2
 Redistribution with MgH₂: 5.4.2.4.3
- C₂H₅MgH**
 Formation: 5.4.2.4.3
- C₂H₆O₂**
 HOCH₂CH₂OH
 Reaction with boric acid: 5.3.2.2.4
- C₂H₆O₄S**
 (CH₃)₂SO₄
 Reaction with B₁₀H₁₃MgI: 5.3.2.7.6
- C₂H₆Sr**
 (CH₃)₂Sr
 Formation: 5.4.3.2.1
- C₂H₆Zn**
 (CH₃)₂Zn
 Reaction with Li[AlH₄]: 5.3.3.4.4
 Reaction with BX₃: 5.3.2.3.1
 Reaction with Be[BH₄]₂: 5.4.3.3.1
 Reaction with MgH₂: 5.4.2.4.3
- C₂H₇Al**
 (CH₃)₂AlH
 Hydroalumination reagent: 5.3.3.4.1
 Reaction with HCN: 5.3.3.5.2
- C₂H₇BBr₂S**
 HBr₂B·S(CH₃)₂
 Formation: 5.3.2.5.1
 Hydroborating agent: 5.3.2.5.1
 Hydroboration directive effects: 5.3.2.5.1
 Hydroboration of alkynes: 5.3.2.5.1
- C₂H₇BCl₂S**
 HCl₂B·S(CH₃)₂
 Formation: 5.3.2.5.1
 Hydroborating agent: 5.3.2.5.1
 Hydroboration directive effects: 5.3.2.5.1
- C₂H₇BI₂S**
 HI₂B·S(CH₃)₂
 Formation: 5.3.2.5.1
 Hydroborating agent: 5.3.2.5.1
 Hydroboration directive effects: 5.3.2.5.1
- C₂H₇B₃**
 nido-1,2-C₂B₃H₇
 Formation: 5.3.2.7.3
 Reaction with acetylene: 5.3.2.7.3
- C₂H₇B₃Si**
 1-H₃Si-1,5-C₂B₃H₄
 Formation: 5.3.2.7.6
- C₂H₇B₄Na**
 Na[C₂B₄H₇]
 Reaction with H₃GeX: 5.3.12.3
 Reaction with R₃GeX: 5.3.12.3
 Reaction with PbBr₂: 5.3.22.3.2
 Reaction with R₃PbCl: 5.3.22.3.2
 Reaction with SiX₄: 5.3.7.3.2
 Reaction with SnCl₂: 5.3.17.3.2
 Reaction with R₃SnX: 5.3.17.3.2
- C₂H₇B₅**
 closo-2,3-C₂B₅H₇
 Formation: 5.3.2.7.3
 closo-2,4-C₂B₅H₇
 Alkylation of: 5.3.2.7.2
 Formation: 5.3.2.7.3
 Hydroboration reagent: 5.3.2.7.1
- C₂H₇GaO**
 (H₃C)₂GaOH
 Formation: 5.3.4.2.5
- C₂H₇InO₂**
 C₂H₅In(OH)₂
 Formation: 5.3.5.2.8
- C₂H₇KZn**
 K[(CH₃)₂ZnH]
 Reaction with H₃Al·THF: 5.3.3.4.4

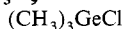
- C₂H₇LiZn**
Li[(CH₃)₂ZnH]
Reaction with H₃Al·THF: 5.3.3.4.4
- C₂H₇N₂Tl**
(CH₃)₂TlHN₂
Reaction with alkynes: 5.3.6.4.1
- C₂H₇NaZn**
Na[(CH₃)₂ZnH]
Reaction with H₃Al·THF: 5.3.3.4.4
- C₂H₈AlN**
H₂AlN(CH₃)₂
Reactivity towards R₂M: 5.3.3.4.4
- C₂H₈BBrS**
H₂BrB·S(CH₃)₂
Formation: 5.3.2.5.1
Hydroborating agent: 5.3.2.5.1
Hydroboration directive effects: 5.3.2.5.1
Hydroboration of alkenes: 5.3.2.5.1
- C₂H₈BClS**
H₂ClB·S(CH₃)₂
Formation: 5.3.2.5.1
Hydroborating agent: 5.3.2.5.1
Hydroboration directive effects: 5.3.2.5.1
- C₂H₈BIS**
H₂IB·S(CH₃)₂
Formation: 5.3.2.5.1
Hydroborating agent: 5.3.2.5.1
Hydroboration directive effects: 5.3.2.5.1
Hydroboration of alkenes: 5.3.2.5.1
- C₂H₈B₄**
nido-C₂B₄H₈
Formation: 5.3.2.7.3
2,3-C₂B₄H₈
Formation: 5.3.2.7.3
Hydroboration reagent: 5.3.2.7.1
- C₂H₈B₁₀O₂**
1,10-(OC)₂B₁₀H₈
Formation: 5.3.2.7.5
- C₂H₈Li₂Mg**
Li₂MgH₂(CH₃)₂
Formation: 5.4.2.4.3
- C₂H₉BS**
H₃B·S(CH₃)₂
Hydroborating agent: 5.3.2.5.1
- C₂H₉B₈Li**
Li[1,10-C₂B₈H₉]
Reaction with 2,3-C₂B₉H₁₁: 5.3.2.7.6
- C₂H₁₀AlLiZn**
Li[(CH₃)₂ZnH₂AlH₂]
Formation: 5.3.3.4.4
- C₂H₁₀B₂**
CH₃HBH₂BHCH₃
Redistribution: 5.3.2.5.3
- (CH₃)₂BH₂BH₂
Redistribution: 5.3.2.5.3
- C₂H₅HBH₂BH₂**
Redistribution: 5.3.2.5.3
- C₂H₁₀B₄Ge**
H₃GeC₂B₄H₇
Formation: 5.3.12.3
- C₂H₁₀B₄Si**
μ-H₃SiC₂B₄H₇
Formation: 5.3.7.3.2
Isomerisation: 5.3.7.3.2
- C₂H₁₀B₅**
B-CH₃-closo-CB₅H₇
Formation: 5.3.2.7.6
- C₂H₁₀B₁₂O₂**
1,12-(OC)₂B₁₂H₁₀
Formation: 5.3.2.7.5
1,7-(OC)₂B₁₂H₁₀
Formation: 5.3.2.7.5
- C₂H₁₁B₉**
closo-2,3-C₂B₉H₁₁
Reaction with CH₃Li: 5.3.2.7.6
C₂B₉H₁₁
Metallation by BeR₂: 5.4.3.4.2
2,3-C₂B₉H₁₁
Reaction with Li[1,10-C₂B₈H₉]: 5.3.2.7.6
- C₂H₁₁B₉Ge**
GeC₂B₉H₁₁
Formation: 5.3.12.3
Isomerization: 5.3.12.3
- C₂H₁₁B₉Na**
Na[C₂B₉H₁₁]
Reaction with SnCl₂: 5.3.17.3.2
- C₂H₁₁B₉Na₂**
Na₂[C₂B₉H₁₁]
Reaction with GeI₂: 5.3.12.3
Reaction with Pb(OAc)₂: 5.3.22.4
- C₂H₁₁B₉Pb**
closo-PbC₂B₉H₁₁
Formation: 5.3.22.4
- C₂H₁₁B₉Sn**
SnC₂B₉H₁₁
Formation: 5.3.17.3.2
- C₂H₁₂B₄**
(CH₂)₂B₄H₈
Formation: 5.3.2.7.6
- C₂H₁₂B₁₀**
closo-1,2-C₂B₁₀H₁₂
Alkylation of: 5.3.2.7.2
Formation: 5.3.2.7.3
1,7-C₂B₁₀H₁₂
Alkylation of: 5.3.2.7.2

- C₂H₁₃B₃O**
 B₃H₇·O(CH₃)₂
 Reaction with CO and BF₃: 5.3.2.7.5
- C₂H₁₄B₂Be₂**
 (CH₃BeBH₄)₂
 Formation: 5.4.3.3.1
- C₂H₁₄B₁₀Ge**
 CH₃GeCHB₁₀H₁₀
 Formation: 5.3.12.3
- C₂H₁₅B₅**
 C₂H₅B₅H₁₀
 Formation: 5.3.2.7.1
- C₂H₁₈B₁₀**
 5-C₂H₅B₁₀H₁₃
 Formation: 5.3.2.7.6
- C₂H₁₈B₁₀Ge**
 (CH₃)₂GeB₁₀H₁₂
 Formation: 5.3.12.3
- C₂H₁₈B₁₀S**
 [(CH₃)₂S]B₁₀H₁₂
 Reaction with alkynes: 5.3.2.7.3
 Reaction with cyclohexene: 5.3.2.7.1
- C₂H₁₈B₁₀Sn**
 (CH₃)₂SnB₁₀H₁₂
 Formation: 5.3.17.3.2
- C₂H₂₂B₆Be₂**
 (CH₃BeB₃H₈)₂
 Formation: 5.4.3.3.1
- C₃Al₄**
 Al₄C₃
 Formation: 5.3.3.5.3
- C₃B₄F₈**
 (F₃B)₂C≡C≡C(BF₂)₂
 Formation: 5.3.2.3.4
- C₃B₁₀Cl₇Cs₂N₃**
 Cs₂[B₁₀Cl₇(CN)₃]
 Formation: 5.3.2.7.4
- C₃Cl₉O₆Tl**
 Tl(O₂CCl₃)₃
 Thallating agent: 5.3.6.3.4
- C₃F₄O₉S₃Tl**
 Tl(O₃SCF₃)₃
 Preparation: 5.3.6.3.4
 Thallating agent: 5.3.6.3.4
- C₃H₃BrMg**
 CH₂=C=CHMgBr
 Equilibrium with propargylmagnesium bromide: 5.4.2.2.1
 HC≡CCH₂MgBr
 Equilibrium with allenylmagnesium: 5.4.2.2.1
- C₃H₃Li**
 Li≡CCH₃
 Reaction with B₅H₉: 5.3.2.7.4
 Reaction with Me₂AlC≡CMe: 5.3.3.5.4
- C₃H₄Br₂Mg₂**
 CH₂CH(MgBr)CH(MgBr)
 Formation: 5.4.2.2.1
- C₃H₄IN**
 ICH₂CH₂CN
 Electrolysis at an In metal cathode: 5.3.5.2.8
 ICH₂CH₂CN
 Electrolysis at a Ga metal cathode: 5.3.4.2.5
 Reaction with Tl metal: 5.3.6.2.9
- C₃H₄Li₂S**
 Li₂(CH₂CHCHS)
 Reaction with MgX₂: 5.4.2.3.1
- C₃H₄MgS**
 Mg(CH₂CHCHS)
 Formation: 5.4.2.3.1
- C₃H₅BCl₂**
 cyclo-C₃H₅BCl₂
 Formation: 5.3.2.3.1
- C₃H₅BrMg**
 CH₂=CHCH₂MgBr
 Formation: 5.4.2.2.1
 Reaction with (CO)₄CoSiPh₃: 5.4.4.5
 Reaction with olefins: 5.4.2.5.1
- C₃H₅CIMg**
 CH₂=CHCH₂MgCl
 Formation: 5.4.2.2.1
 Reaction with R₃GeH: 5.4.5.3
- C₃H₅Cl₂Tl**
 CH₃CH=CHTlCl₂
 Formation: 5.3.6.3.3
- C₃H₆**
 CH₃CH=CH₂
 Reaction with (H₃O)₂B₁₂H₁₂·5 H₂O: 5.3.2.7.1
- C₃H₆AlN**
 (CH₃)₂AlCN
 Formation: 5.3.3.5.2
- C₃H₆BCIN₂**
 (CH₂)₃NBCl
 Reaction with Li[R₃Sn]: 5.3.17.2.2
- C₃H₆B₂Cl₄**
 cyclo-C₃H₆(BCl₂)₂
 Formation: 5.3.2.3.4
- C₃H₆Br₂Hg₂**
 BrHgCH₂CH₂CH₂HgBr
 Formation: 5.4.2.2.2
 Reaction with Mg metal: 5.4.2.2.2
- C₃H₆Br₂Mg₂**
 BrMgCH₂CH₂CH₂MgBr
 Formation: 5.4.2.2.1, 5.4.2.2.2, 5.4.2.3.2
- C₃H₇BCl₂**
 C₃H₇BCl₂
 Formation: 5.3.2.3.6

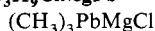
- C₃H₇BO₂**
 $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OBH}$
 Hydroborating agent: 5.3.2.5.1
- C₃H₇B₃**
 nido-2,3,4-C₃B₃H₇
 Formation: 5.3.2.7.3
- C₃H₇BrMg**
 i-C₃H₇MgBr
 Formation: 5.4.2.2.1
 Reaction with olefins: 5.4.2.5.1
 n-C₃H₇MgBr
 Reaction with olefins: 5.4.2.5.3
- C₃H₇Br₂In**
 n-C₃H₇InBr₂
 Formation: 5.3.5.3.3
- C₃H₇CaI**
 C₃H₇CaI
 Formation: 5.4.3.2.1
- C₃H₇ClMg**
 i-C₃H₇MgCl
 Reaction with R₃SnH: 5.4.6.5
- C₃H₇Cl₂Ga**
 n-C₃H₇GaCl₂
 Formation: 5.3.4.4.1
- C₃H₇I₂In**
 n-C₃H₇InI₂
 Formation: 5.3.5.3.3
- C₃H₈B₄FeO₃**
 $(\text{OC})_3\text{FeB}_4\text{H}_8$
 Reaction with alkynes: 5.3.2.7.3
- C₃H₈B₉Br₇**
 C₂H₅(CH₃)B₉Br₇
 Formation: 5.3.2.7.6
- C₃H₈Mg**
 $[(\text{CH}_3)_2\text{CH}]\text{MgH}$
 Formation: 5.4.2.4.3
- C₃H₉Al**
 $(\text{CH}_3)_3\text{Al}$
 Aluminatation of alkynes: 5.3.3.5.2
 Carbalumination: 5.3.3.5.1
 Carbometallation with TiCl₄: 5.3.3.5.1
 Exchange with R₃Ga: 5.3.3.5.4
 Exchange with R₃B: 5.3.3.5.4
 Formation: 5.3.3.2.3, 5.3.3.3.2, 5.3.3.5.3
 Reaction with GeX₄: 5.3.13.5
 Reaction with Li[R₃Si]: 5.3.8.2.1
 Reaction with R₂Mg: 5.3.3.5.4
 Reaction with R₃Ga: 5.3.4.5.2
 Reaction with R₃SnLi: 5.3.18.3
 Reaction with Na[R₄Al]: 5.3.3.5.4
 Reaction with alkynes: 5.3.3.5.1
 Reactivity towards olefins: 5.3.3.5.1
- Thermal decomposition: 5.3.3.5.3
 Transmetalation: 5.3.3.5.4
- C₃H₉AlO₃**
 $(\text{CH}_3\text{O})_3\text{Al}$
 Formation: 5.3.2.4.3
- C₃H₉Al₂Br₃**
 $(\text{CH}_3)_3\text{Al}_2\text{Br}_3$
 Formation: 5.3.3.2.2
- C₃H₉Al₂Cl₃**
 $(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$
 Formation: 5.3.3.2.2
 Reaction with GeX₄: 5.3.13.5
 Redistribution: 5.3.3.3.2
- C₃H₉B**
 $(\text{CH}_3)_3\text{B}$
 Formation: 5.3.2.3.1, 5.3.3.2.2, 5.3.3.5.4
 Reaction with diborane: 5.3.2.5.3
- C₃H₉BO₂**
 $\text{CH}_3(\text{CH}_2)_2\text{B}(\text{OH})_2$
 Formation: 5.3.2.4.1
- C₃H₉BO₃**
 $\text{B}(\text{OCH}_3)_3$
 Reaction with RMgX: 5.3.2.4.1
 Reaction with K[R₃Si]: 5.3.7.4.3
 Reaction with LiHCl₂ and Li/CH₂Cl₂: 5.3.2.4.1
 Reaction with R₃Al: 5.3.2.4.3
- C₃H₉B₃Cl₃N₃**
 $(\text{CH}_3)_3\text{N}_3\text{B}_3\text{Cl}_3$
 Reactions with K[R₃Si]: 5.3.7.4.1
- C₃H₉B₃O₆**
 $(\text{CH}_3\text{OBO})_3$
 Reaction with R₃Al: 5.3.2.4.3
- C₃H₉B₃Si**
 1-H₂CH₃Si-1,5-C₂B₃H₄
 Formation: 5.3.2.7.6
 2-CH₃-1-H₃Si-1,5-C₂B₃H₃
 Formation: 5.3.2.7.6
- C₃H₉BeLi**
 $\text{LiBe}(\text{CH}_3)_3$
 Formation: 5.4.3.4.4
- C₃H₉BrGe**
 $(\text{CH}_3)_3\text{GeBr}$
 Reaction with Na[B₁₀H₁₃]: 5.3.12.3
- C₃H₉BrMgSn**
 $(\text{CH}_3)_3\text{SnMgBr}$
 Formation: 5.4.6.4
- C₃H₉BrSn**
 $(\text{CH}_3)_3\text{SnBr}$
 Reaction with Na[C₂B₄H₇]: 5.3.17.3.2
- C₃H₉Br₃Ga₂**
 $(\text{CH}_3)_3\text{Ga}_2\text{Br}_3$
 Formation: 5.3.4.2.1

C₃H₉Br₃In₂

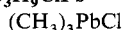
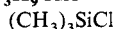
Formation: 5.3.5.2.1

C₃H₉ClGe

Reaction with Carboranes: 5.3.12.3

C₃H₉ClMgPb

Formation: 5.4.7.2.5

C₃H₉ClPbReaction with Na[C₂B₄H₇]: 5.3.22.3.2Reaction with LiB₅H₈: 5.3.22.3.2**C₃H₉ClSi**

Formation: 5.3.2.7.2

Reaction with Al metal: 5.3.8.4

Reaction with LiB₅H₈: 5.3.7.3.2Reaction with GaX₃ and Li metal: 5.3.9

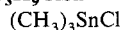
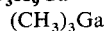
Reaction with Ga and Li metals: 5.3.9

Reaction with InCl₃ and Li metal: 5.3.10

Reaction with RMgX: 5.4.4.2

Reaction with [4-(CH₃)₃SiC₂B₄H₆]⁻:
5.3.7.3.2Reaction with (R₂N)₂BX: 5.3.7.3.1

Reaction with Mg metal: 5.4.4.3

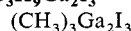
C₃H₉ClSnReaction with LiB₅H₈: 5.3.17.3.2Reaction with 1,2-C₆H₄(MgBr)₂:
5.4.2.2.1**C₃H₉Ga**Formation: 5.3.4.2.2, 5.3.4.2.3, 5.3.4.2.5,
5.3.4.3.1Reaction with R₂Be: 5.3.4.5.2Reaction with R₃Al: 5.3.4.5.2Reaction with R₅As: 5.3.4.5.4Reaction with R₃P=C=PR₃: 5.3.4.5.1Reaction with LiSnR₃: 5.3.19Reaction with H₂: 5.3.4.4.1

Reaction with alkynes: 5.3.4.5.1

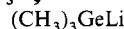
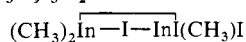
Reaction with carboranes: 5.3.4.4.2

Reaction with cyanide anion: 5.3.4.5.3

Reaction with potassium metal: 5.3.4.5.4

C₃H₉Ga₂I₃

Formation: 5.3.4.2.1

C₃H₉GeLiReaction with (R₂N)₂BX: 5.3.12.2.1**C₃H₉I₃In₂**

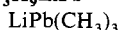
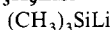
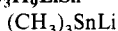
Formation: 5.3.5.3.2

C₃H₉In

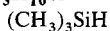
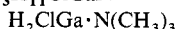
Formation: 5.3.5.2.3, 5.3.5.2.5, 5.3.5.3.1

Reaction with InX₃: 5.3.5.3.2Reaction with Me₃P=CH₂: 5.3.5.4.2Reaction with HNR₂: 5.3.5.4.2Reaction with LiSnR₃: 5.3.20Reaction with C₅H₆: 5.3.5.4.2

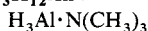
Reaction with alkynes: 5.3.5.4.2

C₃H₉LiPbReaction with (R₂N)₂BX: 5.3.22.2**C₃H₉LiSi**Reaction with B(OR)₃: 5.3.7.4.3Reaction with C₈H₁₄BOMe: 5.3.7.4.3Reaction with [(CH₃)₃C]₃BB(OCH₃):
5.3.7.4.3Reaction with (R₂N)₂BX: 5.3.7.4.1Reaction with (C₈H₁₄BH)₂: 5.3.7.4.2**C₃H₉LiSn**Reaction with AlR₃ or R₂AlX: 5.3.18.3Reaction with BH₃: 5.3.17.2.1Reaction with (R₂N)₂BX and R₂NBX₂:
5.3.17.2.2Reaction with GaR₃: 5.3.19Reaction with InR₃: 5.3.20Reaction with TiR₃: 5.3.21.2**C₃H₉O₃P**Reaction with RTiX₂: 5.3.6.3.7**C₃H₉Tl**

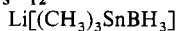
Formation: 5.3.6.3.2

Reaction with Hg(SiR₃)₂: 5.3.11.2Reaction with Li[R₃Sn]: 5.3.21.2Reaction with R₃SnH: 5.3.21.1Reaction with C₅H₆: 5.3.6.4.1**C₃H₁₀Si**Reaction with GaCl₃: 5.3.4.4.1**C₃H₁₁ClGaN**

Reaction with RLi: 5.3.4.4.1

C₃H₁₂AlNReactivity towards R₂M: 5.3.3.4.4

Redistribution: 5.3.3.4.3

C₃H₁₂BLiSn

Formation: 5.3.17.2.1

C₃H₁₂B₂
 (CH₃)₂BH₂BHCH₃
 Redistribution: 5.3.2.5.3

C₃H₁₂GaN
 (CH₃)₃N·GaH₃
 Formation: 5.3.4.4.1

C₃H₁₂GaN
 H₃Ga·N(CH₃)₃
 Reaction with Me₃N·GaMe₃: 5.3.4.4.1
 Reaction with R₂Hg: 5.3.4.4.1

C₃H₁₃B₅
 2-CH₂=CHCH₂B₅H₈
 Formation: 5.3.2.7.6
 2-C₂H₅-2-nido-CB₅H₈
 Formation: 5.3.2.7.4

C₃H₁₄B₉Li
 Li[10-CH₃-nido-7,9-C₂B₉H₁₁]
 Formation: 5.3.2.7.6

C₃H₁₄B₁₀OS
 1,6-Me₂SB₁₀H₈CO
 Formation: 5.3.2.7.5

C₃H₁₆B₅ClSi
 [(ClCH₂)(CH₃)₂Si]B₅H₈
 Rearrangement: 5.3.2.7.6
 [Cl(CH₃)₂SiCH₂]B₅H₈
 Formation: 5.3.2.7.6

C₃H₁₇B₅Pb
 μ-(CH₃)₃PbB₅H₈
 Formation: 5.3.22.3.2

C₃H₁₇B₅Sn
 μ-(CH₃)₃SnB₅H₈
 Formation: 5.3.17.3.2

C₃H₁₈B₁₀
 CH₂=CHCH₂B₁₀H₁₃
 Formation: 5.3.2.7.6

C₃H₂₂B₁₀Si
 (CH₃)₃SiB₁₀H₁₃
 Formation: 5.3.7.3.2

C₃Mg₂
 Mg₂C₃
 Formation: 5.4.2.4.1

C₄BClF₆
 (CF₂=CF)₂BCl
 Formation: 5.3.2.3.1

C₄H₃BCl₂S
 CHCHCHSCBCl₂
 Formation: 5.3.2.3.1

C₄H₃BrMgS
 3-C₄H₃SMgBr
 Formation: 5.4.2.3.1

C₄H₃Cl₂GaS
 SCH=CHCH=CGaCl₂
 Reaction with RMgX: 5.3.4.3.1

C₄H₃ISSr
 2-C₄H₃SSrI
 Formation: 5.4.3.2.1

C₄H₃LiS
 3-(C₄H₃S)Li
 Reaction with MgX₂: 5.4.2.3.1

C₄H₄N
 CH=CHCH=CH
 Problems in RMgX formation: 5.4.2.2.1

C₄H₄O
 CH=CHCH=CHO
 Alumination: 5.3.3.5.2

C₄H₄S
 CH=CHCH=CHS
 Alumination: 5.3.3.5.2
 Metallation by RCaX: 5.4.3.4.2
 Reaction with Ti(O₂CCF₃)₃: 5.3.6.3.4

C₄H₅BO₃
 2-(OH)₂B-cyclo-C₄H₃O
 Formation: 5.3.2.4.1

C₄H₆
 CH₃C≡CCH₃
 Reaction with BF₃: 5.3.2.3.4
 H₂C=CHCH=CH₂
 Reaction with R₃AlNa in THF: 5.3.3.5.4

C₄H₆BCl
 (CH₂=CH)₂BCl
 Formation: 5.3.2.3.1

C₄H₆BN
 H₂BNCHCHCHCH
 Hydroboration of alkenes: 5.3.2.5.1

C₄H₆B₂
 nido-C₄B₂H₆
 Formation: 5.3.2.7.3

C₄H₆CITl
 (CH₂=CH)₂TlCl
 Formation: 5.3.6.3.3

C₄H₆GaKN₂
 K[(CH₃)₂Ga(CN)₂]
 Formation: 5.3.4.5.3

C₄H₆Hg
 (CH₂=CH)₂Hg
 Reaction with Al metal: 5.3.3.2.3
 Reaction with Li[AlH₄]: 5.3.3.4.4
 Reaction with BX₃: 5.3.2.3.1
 Reaction with H₃Al·NMe₃: 5.3.3.4.4
 Reaction with BX₃: 5.3.2.3.1

C₄H₆LiS
 Li₂[CH₂C(CH₃)CHS]
 Reaction with MgX₂: 5.4.2.3.1

C₄H₆Mg
 CH₂CH=CHCH₂Mg
 Formation: 5.4.2.2.4

- C₄H₆MgS**
Mg[CH₂C(CH₃)CHS]
Formation: 5.4.2.3.1
- C₄H₆N₂O₂**
C₂H₅OC(O)CHN₂
Reaction with RBCl₂, R₂BCl: 5.3.2.3.5
- C₄H₆O₄Pb**
Pb(O₂CCH₃)₂
Reaction with Na₂[C₂B₉H₁₁]: 5.3.22.4
- C₄H₇Al**
(CH₃)₂AlC≡CH
Reaction with R₂AlH: 5.3.3.4.1, 5.3.3.5.4
- C₄H₇BO₂**
CH₂=CHBOCH₂CH₂O
Reaction with dienes: 5.3.2.6.4
- C₄H₇BO₂S**
2-(HO)₂B-cyclo-C₄H₅S
Formation: 5.3.2.4.1
- C₄H₇ClMg**
CH₂CH₂C(CH₃)MgCl
Formation: 5.4.2.5.1
- C₄H₇Cl₂Mg**
CH₂=C(CH₃)CH₂MgCl₂
Reaction with olefins: 5.4.2.5.1
- C₄H₇Tl**
(CH₃)₂TlC≡CH
Formation: 5.3.6.4.1
- C₄H₉BCl**
(CH₂)₄BCl
Reaction with Na-K alloy: 5.3.2.3.2
- C₄H₉Cl₂Si**
(CH₂)₄SiCl₂
Reaction with NaC₂B₄H₇: 5.3.7.3.2
- C₄H₉Mg**
(CH₂)₄Mg
Formation: 5.4.2.3.2
- C₄H₉MgO**
CH₂CH₂CH₂CH₂OMg
Formation: 5.4.2.2.1
- C₄H₉BI₂**
n-C₄H₉BI₂
Formation: 5.3.2.3.1
- C₄H₉BeCl**
(CH₃)₃CBeCl
Formation: 5.4.3.3.2
- C₄H₉BrMg**
n-C₄H₉MgBr
Formation: 5.4.2.2.1
Reaction with BeCl₂: 5.4.3.3.1
- C₄H₉Br₂In**
n-C₄H₉InBr₂
Formation: 5.3.5.3.3
- C₄H₉CaI**
n-C₄H₉CaI
Polymerization of dienes: 5.4.3.4.1
- C₄H₉ClMg**
(CH₃)₃CMgCl
Formation: 5.4.2.2.1
Reaction with AlCl₃: 5.3.3.3.1
Reaction with BeCl₂: 5.4.3.3.1
Reaction with olefins: 5.4.2.5.1
- C₂H₅(CH₃)CHMgCl
Formation: 5.4.2.2.1
Reaction with R₃SnH: 5.4.6.5
- C₄H₉CuO**
Cu[OC(CH₃)₃]
Reaction with alkynes: 5.4.2.4.1
- C₄H₉F₃Sn**
CF₃Sn(CH₃)₃
Reaction with BX₃: 5.3.2.3.1
- C₄H₉GeN**
(CH₃)₃GeCN
Reaction with R₃Ga: 5.3.4.5.3
- C₄H₉IMg**
n-C₄H₉MgI
Formation: 5.4.2.3.1
Reaction with BeCl₂: 5.4.3.3.1
- C₄H₉I₂In**
n-C₄H₉InI₂
Formation: 5.3.5.3.3
- C₄H₉Li**
CH₃(CH₂)₃Li
Reaction with MgH₂: 5.4.2.4.3
(CH₃)₃CLi
Reaction with BX₃: 5.3.2.4
Reaction with AlCl₃: 5.3.3.3.1
- C₂H₅(CH₃)CHLi
Reaction with MgX₂: 5.4.2.3.1
Reaction with H₃B·THF: 5.3.2.5.2
Reaction with MgX₂: 5.3.2.3.1
Reaction with BX₃: 5.3.2.3.1
- C₄H₉NPb**
(CH₃)₃PbCN
Reaction with R₃Ga: 5.3.4.5.3
- C₄H₉NSi**
(CH₃)₃SiNC
Reaction with BX₃: 5.3.2.3.1
- C₄H₉NSn**
(CH₃)₃SnCN
Reaction with R₃Ga: 5.3.4.5.3
- C₄H₉Na**
Na[C₄H₉-n]
Reaction with MgX₂: 5.4.2.3.1
- C₄H₁₀AlBr**
(C₂H₅)₂AlBr
Formation: 5.3.4.3.1

- Reaction with $\text{Li}[\text{Ph}_3\text{Si}]$: 5.3.8.2.1
- $\text{C}_4\text{H}_{10}\text{AlCl}$**
 $(\text{C}_2\text{H}_5)_2\text{AlCl}$
 Complex with KCl : 5.3.3.3.2
 Formation: 5.3.3.3.2, 5.3.3.3.4
 Reaction with $[\text{AlR}_4]^-$: 5.3.3.3.2
 Reaction with GaX_3 : 5.3.4.3.1
 Reaction with $\text{Li}[\text{R}_3\text{Si}]$: 5.3.8.2.1
 Reaction with NaH : 5.3.3.3.3
 Reaction with R_3SnLi : 5.3.18.3
 Reaction with SnF_2 : 5.3.18.4
 Redistribution: 5.3.3.3.2
- $\text{C}_4\text{H}_{10}\text{AlClF}_2\text{Sn}$**
 $(\text{C}_2\text{H}_5)_2\text{AlSnClF}_2$
 Formation: 5.3.18.4
- $\text{C}_4\text{H}_{10}\text{AlCl}_2\text{K}$**
 $\text{K}[(\text{C}_2\text{H}_5)_2\text{AlCl}_2]$
 Formation: 5.3.4.3.1, 5.3.4.4.1
- $\text{C}_4\text{H}_{10}\text{AlI}$**
 $(\text{C}_2\text{H}_5)_2\text{AlI}$
 Reaction with CH_2N_2 : 5.3.3.5.5
- $\text{C}_4\text{H}_{10}\text{BBr}$**
 $(\text{C}_2\text{H}_5)_2\text{BBr}$
 Formation: 5.3.2.3.1
- $\text{C}_4\text{H}_{10}\text{BCl}$**
 $(\text{C}_2\text{H}_5)_2\text{BCl}$
 Formation: 5.3.2.3.1, 5.3.2.3.6
 Reaction with Li/THF : 5.3.2.3.2
 Reaction with borates: 5.3.2.3.2
- $\text{C}_4\text{H}_{10}\text{BCIN}$**
 $(\text{C}_2\text{H}_5)_2\text{NBCl}$
 Reaction with $\text{Li}[\text{R}_3\text{Sn}]$: 5.3.17.2.2
- $\text{C}_4\text{H}_{10}\text{BCIN}_2$**
 $\text{CH}_3\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)\text{BCl}$
 Reaction with $\text{Li}[\text{R}_3\text{Pb}]$: 5.3.22.2
- $\text{C}_4\text{H}_{10}\text{BClO}$**
 $\text{H}_2\text{ClB}\cdot\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$
 Monohydroboration of alkynes: 5.3.2.5.1
- $\text{C}_4\text{H}_{10}\text{BF}_3\text{O}$**
 $\text{F}_3\text{B}\cdot\text{O}(\text{C}_2\text{H}_5)_2$
 Reaction with R_3Al : 5.3.2.3.1
- $\text{C}_4\text{H}_{10}\text{BI}$**
 $(\text{C}_2\text{H}_5)_2\text{BI}$
 Formation: 5.3.2.3.1
- $\text{C}_4\text{H}_{10}\text{B}_4\text{Pb}$**
 $\text{closo-Pb}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$
 Formation: 5.3.22.3.2
- $\text{C}_4\text{H}_{10}\text{B}_4\text{Sn}$**
 $(\text{CH}_3)_2\text{SnC}_2\text{B}_4\text{H}_4$
 Formation: 5.3.17.3.2
- $\text{C}_4\text{H}_{10}\text{BaO}_2$**
 $\text{Ba}(\text{OC}_2\text{H}_5)_2$
 Reaction with AlR_3 : 5.4.3.3.1
- $\text{C}_4\text{H}_{10}\text{Be}$**
 $(\text{CH}_3)_2\text{CHCH}_2\text{BeH}$
 Reaction with olefins: 5.4.3.4.3
 $(\text{CH}_3)_3\text{CBeH}$
 Formation: 5.4.3.3.2
 $(\text{C}_2\text{H}_5)_2\text{Be}$
 Addition to olefins: 5.4.3.4.1
 Catalyst for formation of R_2Be : 5.4.3.2.2
 Dimerization of propene: 5.4.3.4.1
 Formation: 5.4.3.3.1, 5.4.3.4.3
 Reaction with HgR_2 : 5.4.3.4.4
 Reaction with $\text{Be}(\text{SEt})_2$: 5.4.3.3.2
 Reaction with BR_3 : 5.4.3.4.4
 Redistribution with BeX_2 : 5.4.3.3.2
- $\text{C}_4\text{H}_{10}\text{BeO}_2$**
 $\text{Be}[\text{OC}_2\text{H}_5]_2$
 Reaction with MgR_2 : 5.4.3.3.1
- $\text{C}_4\text{H}_{10}\text{BeS}_2$**
 $(\text{SC}_2\text{H}_5)_2\text{Be}$
 Reaction with BeR_2 : 5.4.3.3.2
- $\text{C}_4\text{H}_{10}\text{CaO}_2$**
 $\text{Ca}(\text{OC}_2\text{H}_5)_2$
 Reaction with AlR_3 : 5.4.3.3.1
- $\text{C}_4\text{H}_{10}\text{Cd}$**
 $(\text{C}_2\text{H}_5)_2\text{Cd}$
 Reaction with R_2AlH : 5.3.3.4.4
- $\text{C}_4\text{H}_{10}\text{ClGa}$**
 $(\text{C}_2\text{H}_5)_2\text{GaCl}$
 Formation: 5.3.4.3.5
 Reaction with R_2AlH : 5.3.4.4.1
 Reaction with RLi : 5.3.4.3.1
- $\text{C}_4\text{H}_{10}\text{ClIn}$**
 $(\text{C}_2\text{H}_5)_2\text{InCl}$
 Formation: 5.3.5.3.2
- $\text{C}_4\text{H}_{10}\text{Cl}_2\text{Ti}$**
 $(\text{C}_2\text{H}_5)_2\text{TiCl}_2$
 Catalyst for carbalumination of alkynes: 5.3.3.5.1
- $\text{C}_4\text{H}_{10}\text{GaI}$**
 $(\text{C}_2\text{H}_5)_2\text{GaI}$
 Reaction with CH_2N_2 : 5.3.4.3.4
- $\text{C}_4\text{H}_{10}\text{Ga}_2\text{I}_4$**
 $(\text{CH}_3\text{CH}_2)_2\text{Ga}_2\text{I}_4$
 Formation: 5.3.4.2.1
- $\text{C}_4\text{H}_{10}\text{Hg}$**
 $(\text{C}_2\text{H}_5)_2\text{Hg}$
 Formation: 5.4.3.4.4
 Reaction with Al metal: 5.3.3.2.3
 Reaction with Ga metal: 5.3.4.2.3
 Reaction with R_2AlH : 5.3.3.4.4
 Reaction with Be , Ca , Sr and Ba metals: 5.4.3.2.2

- C₄H₁₀In**
 (C₂H₅)₂InI
 Formation: 5.3.5.2.2
- C₄H₁₀ITl**
 (C₂H₅)₂TlI
 Formation: 5.3.6.2.9
- C₄H₁₀LiP**
 (CH₃)₂PCH₂CH₂Li
 Reaction with RMgX: 5.4.2.3.1
- C₄H₁₀Mg**
 (C₂H₅)₂Mg
 Formation: 5.4.2.4.1
 Formation from C₂H₄: 5.4.2.4.1
 Reaction with Li[AlH₄]: 5.4.2.4.1, 5.3.3.4.4
 Reaction with R₂AlH: 5.3.3.4.4
 Reaction with MgX₂: 5.4.2.3.2
 Reaction with olefins: 5.4.2.5.1
 Redistribution with MgH₂: 5.4.2.4.3
 Reaction with B₂H₆: 5.3.2.5.2
- C₄H₁₀O**
 (C₂H₅)₂O
 Base in redistribution: 5.3.3.3.2
 Catalyst for reaction of Ga metal with RX: 5.3.4.2.2
- C₄H₁₀O₂Sr**
 Sr(OC₂H₅)₂
 Reaction with AlR₃: 5.4.3.3.1
- C₄H₁₀O₂Zn**
 (C₂H₅O)₂Zn
 Formation: 5.3.2.4.3
- C₄H₁₀S**
 (CH₃CH₂)₂S
 Catalyst for reaction of Ga metal with RX: 5.3.4.2.2
- C₄H₁₀Zn**
 (C₂H₅)₂Zn
 Catalyst for MgH₂ addition to olefins: 5.4.2.4.1
 Reaction with B(OR)₃: 5.3.2.4.3
 Reaction with R₂AlH: 5.3.3.4.4
 Reaction with Ca, Sr and Ba metals: 5.4.3.2.2
- C₄H₁₁Al**
 (C₂H₅)₂AlH
 Formation: 5.3.3.2.1
 Hydroalumination reagent: 5.3.3.4.1
 Metallation of alkynes: 5.3.3.5.2
 Rate of hydroalumination of alkenes: 5.3.3.4.1
 Rate of hydroalumination of cycloolefins: 5.3.3.4.1
 Reaction with R₂GaCl: 5.3.4.4.1
 Reaction with R₂M: 5.3.3.4.4
- Reaction with HCN: 5.3.3.5.2
 Reaction with C₂H₄: 5.3.3.3.3
- C₄H₁₁AlO**
 $\text{H}_3\text{Al} \cdot \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$
 Reaction with Li[ZnMe₂H]: 5.3.3.4.4
 Reaction with Na[ZnMe₂H]: 5.3.3.4.4
- C₄H₁₁B**
 (C₂H₅)₂BH
 Formation: 5.3.2.5.1
 Hydroboration reagent: 5.3.2.5.1
- C₄H₁₁BCl₂O**
 HCl₂B·O(C₂H₅)₂
 Formation: 5.3.2.5.1
 Hydroborating agent: 5.3.2.5.1
- C₄H₁₁BO**
 $\text{H}_3\text{B} \cdot \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$
 Hydroboration directive effects: 5.3.2.5.1
 Hydroboration reagent: 5.3.2.5.1, 5.3.2.6.1
 Reaction with boron—carbon bonds: 5.3.2.6.1
 Reactivity toward functional groups: 5.3.2.5.1
- C₄H₁₁BOS**
 H₃B·c-SC₄H₈O
 Hydroborating agent: 5.3.2.5.1
- C₄H₁₁BO₂**
 CH₃(CH₂)₃B(OH)₂
 Formation: 5.3.2.4.1
 (CH₃)₂CHCH₂B(OH)₂
 Formation: 5.3.2.4.1
 (CH₃)₃CB(OH)₂
 Formation: 5.3.2.4.1
- C₄H₁₁BS**
 $\text{H}_2\text{B}[(\text{CH}_2)_3\text{SCH}_3]$
 Formation: 5.3.2.5.1
- C₄H₁₁B₄Na**
 Na[(CH₃)₂C₂B₄H₅]
 Reaction with PbBr₂: 5.3.22.3.2
 Reaction with R₃GeX: 5.3.12.3
- C₄H₁₁BeNa**
 Na[BeH(C₂H₅)₂]
 Reaction with olefins: 5.4.3.4.3
- C₄H₁₁Br₂GaSi**
 (CH₃)₃SiCH₂GaBr₂
 Formation: 5.3.4.3.5
- C₄H₁₁ClMgSi**
 (CH₃)₃SiCH₂MgCl
 Reaction with PbX₂: 5.4.7.2.5
- C₄H₁₁ClSi**
 (CH₃)₂Si(C₂H₅)Cl
 Reaction with GaX₃: 5.3.4.3.1

- $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$
 Reaction with B_5H_9 : 5.3.2.7.2
 Reaction with GaX_3 : 5.3.4.3.1
- $\text{C}_4\text{H}_{11}\text{Cl}_2\text{GaSi}$**
 $(\text{CH}_3)_3\text{SiCH}_2\text{GaCl}_2$
 Formation: 5.3.4.3.5
- $\text{C}_4\text{H}_{11}\text{Cl}_2\text{InSi}$**
 $(\text{CH}_3)_3\text{SiCH}_2\text{InCl}_2$
 Formation: 5.3.5.3.2
- $\text{C}_4\text{H}_{11}\text{Ga}$**
 $(\text{C}_2\text{H}_5)_2\text{GaH}$
 Formation: 5.3.4.4.1
 Reaction with alkynes: 5.3.4.4.1
 Reaction with olefins: 5.3.4.4.1
 Safety: 5.3.4.4.1
i- $\text{C}_4\text{H}_9\text{GaH}_2$
 Formation: 5.3.4.4.2
- $\text{C}_4\text{H}_{12}\text{AlClO}$**
 $\text{H}_2\text{ClAl}\cdot\text{O}(\text{C}_2\text{H}_5)_2$
 Reaction with $\text{K}[\text{SiH}_3]$: 5.3.8.2.1
- $\text{C}_4\text{H}_{12}\text{AlNa}$**
 $\text{Na}[(\text{C}_2\text{H}_5)_2\text{AlH}_2]$
 Formation: 5.3.3.4.3
 $\text{Na}[i\text{-C}_4\text{H}_9\text{AlH}_3]$
 Formation: 5.3.3.4.3
- $\text{C}_4\text{H}_{12}\text{BClN}_2$**
 $[(\text{CH}_3)_2\text{N}]_2\text{BCl}$
 Reaction with R_3GeM : 5.3.12.2.1
 Reaction with R_3SiK : 5.3.7.4.1
 Reaction with R_3SiX : 5.3.7.3.1
 Reaction with $\text{Li}[\text{R}_3\text{Sn}]$: 5.3.17.2.2
- $\text{C}_4\text{H}_{12}\text{BClO}$**
 $\text{H}_2\text{ClB}\cdot\text{O}(\text{C}_2\text{H}_5)_2$
 Cyclic hydroboration of α,ω -dienes:
 5.3.2.5.1
 Hydroboration of alkenes, directive effects:
 5.3.2.5.1
- $\text{C}_4\text{H}_{12}\text{B}_2\text{O}_4$**
 $(\text{HO})_2\text{B}(\text{CH}_2)_4\text{B}(\text{OH})_2$
 Formation: 5.3.2.4.1
- $\text{C}_4\text{H}_{12}\text{B}_6$**
 $1,7\text{-(CH}_3)_2\text{-closo-1,7-C}_2\text{B}_6\text{H}_6$
 Formation: 5.3.2.7.3
- $\text{C}_4\text{H}_{12}\text{BeLi}_2$**
 $\text{Li}_2\text{Be}(\text{CH}_3)_4$
 Formation: 5.4.3.4.4
- $\text{C}_4\text{H}_{12}\text{BeN}_2$**
 $\text{Be}[\text{N}(\text{CH}_3)_2]_2$
 Reaction with RLi : 5.4.3.3.1
- $\text{C}_4\text{H}_{12}\text{Cl}_3\text{GaSn}$**
 $(\text{CH}_3)_3\text{SnCl}\cdot\text{GaCH}_3\text{Cl}_2$
 Formation: 5.3.4.3.1
- $\text{C}_4\text{H}_{12}\text{Cl}_4\text{O}_4\text{Si}_4$**
 $(\text{CH}_3\text{SiClO})_4$
 Formation: 5.3.4.3.2
- $\text{C}_4\text{H}_{12}\text{D}_2\text{GaN}$**
 $\text{D}_2\text{CH}_3\text{Ga}\cdot\text{N}(\text{CH}_3)_3$
 Formation: 5.3.4.4.1
- $\text{C}_4\text{H}_{12}\text{GaK}$**
 $\text{K}[(\text{CH}_3)_4\text{Ga}]$
 Formation: 5.3.4.5.4
- $\text{C}_4\text{H}_{12}\text{GaLi}$**
 $\text{Li}[(\text{CH}_3)_4\text{Ga}]$
 Formation: 5.3.4.3.1
 $\text{Li}(7)$ and H NMR : 5.3.4.5.2
 Reaction with potassium metal: 5.3.4.5.4
- $\text{C}_4\text{H}_{12}\text{Ge}$**
 $(\text{CH}_3)_4\text{Ge}$
 Formation: 5.3.3.2.2
 Reaction with GaX_3 : 5.3.4.3.1
- $\text{C}_4\text{H}_{12}\text{LiTi}$**
 $\text{LiTi}(\text{CH}_3)_4$
 Reaction with R_6Sn_2 : 5.3.21.3
- $\text{C}_4\text{H}_{12}\text{Li}_2\text{Zn}$**
 $\text{Li}_2[\text{Zn}(\text{CH}_3)_4]$
 Reaction with MgX_2 : 5.4.2.3.1
- $\text{C}_4\text{H}_{12}\text{MgZn}$**
 $\text{Mg}[\text{Zn}(\text{CH}_3)_4]$
 Formation: 5.4.2.3.1, 5.4.2.4.3
 Reaction with MgH_2 : 5.4.2.4.3
- $\text{C}_4\text{H}_{12}\text{N}_2\text{Sn}$**
 $[(\text{CH}_3)_2\text{N}]_2\text{Sn}$
 Reaction with BX_3 : 5.3.17.4
- $\text{C}_4\text{H}_{12}\text{Si}$**
 $(\text{CH}_3)_4\text{Si}$
 Formation: 5.3.3.2.2
 Reaction with GaX_3 : 5.3.4.3.1
- $\text{C}_4\text{H}_{12}\text{Sn}$**
 $(\text{CH}_3)_4\text{Sn}$
 Formation: 5.3.3.2.2
 Reaction with BX_3 : 5.3.2.3.1
 Reaction with GaX_3 : 5.3.4.3.1
- $\text{C}_4\text{H}_{13}\text{AlO}$**
 $\text{H}_3\text{Al}\cdot\text{O}(\text{C}_2\text{H}_5)_2$
 Reaction with R_3Al : 5.3.3.4.3
- $\text{C}_4\text{H}_{14}\text{AlN}$**
 $\text{CH}_3\text{H}_2\text{Al}\cdot\text{N}(\text{CH}_3)_3$
 Formation: 5.3.3.4.3
- $\text{C}_4\text{H}_{14}\text{Al}_2\text{Na}$**
 $\text{Na}[(\text{CH}_3)_4\text{Al}_2\text{H}_2]$
 Formation: 5.3.3.4.4

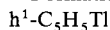
- C₄H₁₄B₂**
 C₂H₅HBH₂BHC₂H₅
 Redistribution: 5.3.2.5.3
 (C₂H₅)₂BH₂BH₂
 Redistribution: 5.3.2.5.3
- C₄H₁₄B₁₀O**
 9-CH₃CO-1,2-C₂B₁₀H₁₁
 Formation: 5.3.2.7.6
- C₄H₁₄GaN**
 H₂CH₃Ga·N(CH₃)₃
 Formation: 5.3.4.4.1
- C₄H₁₄Ga₂**
 [(CH₃)₂GaH]₂
 Formation (claimed): 5.3.4.4.1
- C₄H₁₅AlO₂Si**
 H₂AlSiH₃·DME
 Formation: 5.3.8.2.1
- C₄H₁₅B₇**
 (CH₃)₂-nido-C₂B₇H₉
 Formation: 5.3.2.7.3
- C₄H₁₆B₈**
 5,6-(CH₃)₂-nido-5,6-C₂B₈H₁₀
 Formation: 5.3.2.7.3
- C₄H₁₆B₈Si**
 μ,μ-H₂Si(C₂B₄H₇)₂
 Formation: 5.3.7.3.2, 5.3.7.3.2
- C₄H₁₇B₅**
 2-n-C₄H₉B₅H₈
 Formation: 5.3.2.7.1
- C₄H₁₇B₁₀NO**
 2,7,8-Me₃NB₁₀H₈CO
 Formation: 5.3.2.7.5
- C₄H₁₈B₁₀N₂**
 (CH₃CN)₂B₁₀H₁₂
 Reaction with HC≡CC≡CH: 5.3.2.7.3
- C₄H₁₉B₅**
 (C₂H₅)₂B₅H₉
 Formation: 5.3.2.7.1
- C₄H₂₀B₁₇Li**
 Li[10-[1'-(1',10'-C₂B₈H₉)]-7,9-C₂B₉H₁₁]
 Formation: 5.3.2.7.6
- C₄H₂₂B₁₀**
 C₄H₉B₁₀H₁₃
 Formation: 5.3.2.7.6
- C₄H₂₂B₂₀Hg**
 (1,2-C₂B₁₀H₁₁-9)₂Hg
 Acetylation: 5.3.2.7.6
- C₄H₂₄B₁₀S₂**
 [(CH₃)₂S]₂B₁₀H₁₂
 Reaction with alkynes: 5.3.2.7.3
- C₄HgK₂N₄**
 K₂[Hg(CN)₄]
 Reaction with R₃Ga: 5.3.4.5.3
- C₅Cl₅Tl**
 Tl[C₅Cl₅]
 Formation: 5.3.6.2.1, 5.3.6.3.4
- C₅D₅Tl**
 C₅D₅Tl
 Formation: 5.3.6.3.4
- C₅HD₄Tl**
 C₅D₄HTl
 Formation: 5.3.6.3.4
- C₅H₄B₂Br₄**
 2,5-C₅H₄(BBr₂)₂
 Formation: 5.3.2.3.1
- C₅H₄BrMgN**
 2-BrMgC₅H₄N
 Formation: 5.4.2.2.1
- C₅H₅BeBr**
 h¹-C₅H₅BeBr
 Formation: 5.4.3.3.2
- C₅H₅BeCl**
 h¹-C₅H₅BeCl
 Formation: 5.4.3.3.2
 h⁵-C₅H₅BeCl
 Reaction with LiPh: 5.4.3.3.1
- C₅H₅BeI**
 h¹-C₅H₅BeI
 Formation: 5.4.3.3.2
- C₅H₅BrMg**
 C₅H₅MgBr
 Pyrolysis: 5.4.2.3.2
- C₅H₅Cl₃Ti**
 C₅H₅TiCl₃
 Catalyst in formation of Cp₂Mg:
 5.4.2.2.5
- C₅H₅I₂In**
 h¹-C₅H₅InI₂
 Formation: 5.3.5.3.2
- C₅H₅In**
 h¹-C₅H₅In
 Formation: 5.3.5.3.1
 h⁵-C₅H₅In
 Formation: 5.3.5.2.4
 Reaction with Tl metal: 5.3.6.2.7
- C₅H₅Li**
 C₅H₅Li
 Reaction with InX₃, R₂InX, InX: 5.3.5.3.1
- C₅H₅N**
 C₅H₅N
 Base in redistribution: 5.3.3.3.2
 Reaction with MgH₂: 5.4.2.4.1
- C₅H₅Na**
 Na[C₅H₅]
 Reaction with InX₃, R₂InX: 5.3.5.3.1
 Reaction with R₂GaX: 5.3.4.3.1

C₅H₅Tl

Formation: 5.3.6.3.4



Formation: 5.3.6.2.7

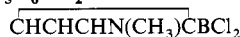


Formation: 5.3.6.2.2, 5.3.6.2.3

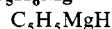
C₅H₆

Reaction with In metal: 5.3.5.2.4

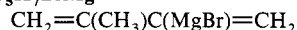
Reaction with Ca metal: 5.4.3.2.3

C₅H₆BCl₂N

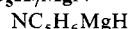
Formation: 5.3.2.3.1

C₅H₆Mg

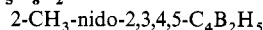
Formation: 5.4.2.4.2, 5.4.2.4.3

C₅H₇BrMg

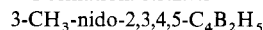
Formation: 5.4.2.2.1

C₅H₇MgN

Formation: 5.4.2.4.1

C₅H₈B₂

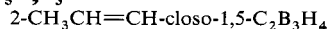
Formation: 5.3.2.7.3



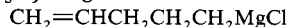
Formation: 5.3.2.7.3

C₅H₉Al

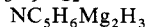
Reaction with LiC≡CMe: 5.3.3.5.4

Reaction with M(C≡CMe)₂: 5.3.3.5.4**C₅H₉B₃**

Formation: 5.3.2.7.1

C₅H₉ClMg

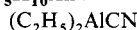
Formation: 5.4.2.2.1

C₅H₉Mg₂N

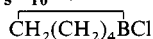
Formation: 5.4.2.4.1

C₅H₉O₄TlReaction with P(OR)₃: 5.3.6.3.7**C₅H₉Tl**

Formation: 5.3.6.4.1

C₅H₁₀AlN

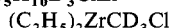
Formation: 5.3.3.5.2

C₅H₁₀BCl

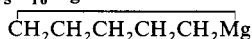
Formation: 5.3.2.5.1

C₅H₁₀Br₂Mg₂

Formation: 5.4.2.3.2

C₅H₁₀D₃ClZr

Carbalumination: 5.3.3.5.1

C₅H₁₀Mg

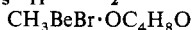
Formation: 5.4.2.2.2, 5.4.2.3.2

Redistribution with MgX₂: 5.4.2.3.2**C₅H₁₁BO**

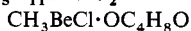
Formation: 5.3.2.6.1

C₅H₁₁BeBr

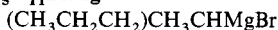
Redistribution: 5.4.3.3.2

C₅H₁₁BeBrO₂

Formation: 5.4.3.3.2

C₅H₁₁BeClO₂

Formation: 5.4.3.3.2

C₅H₁₁BrMg

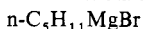
Formation: 5.4.2.2.1



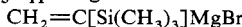
Formation: 5.4.2.2.1



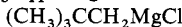
Formation: 5.4.2.2.1



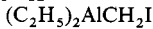
Formation: 5.4.2.2.1

C₅H₁₁BrMgSi

Formation: 5.4.2.2.1

C₅H₁₁ClMg

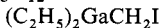
Formation: 5.4.2.2.1

Reaction with PbX₂: 5.4.7.2.5Reaction with BeCl₂: 5.4.3.3.1**C₅H₁₂AlI**

Formation: 5.3.3.5.5

C₅H₁₂Be

Formation: 5.4.3.3.2

C₅H₁₂Gal

Formation: 5.3.4.3.4

Reaction with RMgX: 5.3.4.3.4

C₅H₁₂Hg₂Reaction with Mg/MgX₂: 5.4.2.3.2

- C₅H₁₂Mg**
CH₃MgCH(CH₃)C₂H₅
Formation: 5.4.2.3.1
- C₅H₁₂N₂**
[(CH₃)₄N][CN]
Reaction with R₃Ga: 5.3.4.5.3
- C₅H₁₂Si**
(CH₃)₃SiCH=CH₂
Reaction with R₂AlH: 5.3.3.4.1
Reaction with R₃Al: 5.3.3.4.2
Reaction with H₂ and Al metal: 5.3.3.2.1
- C₅H₁₃B₃Be**
h¹-C₅H₅BeB₃H₈
Formation: 5.4.3.3.1
- C₅H₁₃B₅Be**
h⁵-C₅H₅BeB₅H₈
Formation: 5.4.3.3.1
- C₅H₁₄BN**
H₂B(CH₂)₃N(CH₃)₂
Formation: 5.3.2.5.1
- C₅H₁₄B₂O₄**
(CH₃O)₂BCH₂B(OCH₃)₂
Formation: 5.3.2.3.2, 5.3.2.4.1
(HO)₂B(CH₂)₅B(OH)₂
Formation: 5.3.2.4.1
- C₅H₁₄Si**
(CH₃)₃SiC₂H₅
Reaction with GaX₃: 5.3.4.3.1
- C₅H₁₅AlMg**
CH₃Mg[(CH₃)₄Al]
Formation: 5.3.3.5.4
- C₅H₁₅As**
(CH₃)₅As
Reaction with R₃Ga: 5.3.4.5.4
- C₅H₁₅B₄ClSi**
4-[ClCH₂Si(CH₃)₂]-nido-2,4-C₂B₄H₇
Rearrangement: 5.3.2.7.6
4-(ClMe₂SiCH₂)-nido-C₂B₄H₇
Formation: 5.3.2.7.6
- C₅H₁₅B₅Be**
h¹-C₅H₅BeB₅H₁₀
Formation: 5.4.3.3.1
- C₅H₁₅BeLi₃**
Li₃Be(CH₃)₅
Formation: 5.4.3.4.4
- C₅H₁₅BeN**
(CH₃)₂Be·N(CH₃)₃
Redistribution with BeR₂: 5.4.3.4.4
- C₅H₁₅Be₂Li**
LiBe₂(CH₃)₅
Formation: 5.4.3.4.4
- C₅H₁₅DGaN**
(CH₃)₂DGa·N(CH₃)₃
Formation: 5.3.4.4.1
- C₅H₁₆AlN**
C₂H₅H₂Al·N(CH₃)₃
Formation: 5.3.3.4.3
H(CH₃)₂Al·N(CH₃)₃
Formation: 5.3.3.4.3
- C₅H₁₆B₄Ge**
(CH₃)₃GeC₂B₄H₇
Formation: 5.3.12.3
- C₅H₁₆B₄Pb**
μ-(CH₃)₃PbC₂B₄H₇
Formation: 5.3.22.3.2
- C₅H₁₆B₄Si**
(CH₃)₃SiC₂B₄H₇
Deprotonation: 5.3.7.3.2
Isomerisation: 5.3.7.3.2
- C₅H₁₆B₄Sn**
μ-(CH₃)₃SnC₂B₄H₇
Formation: 5.3.17.3.2
- C₅H₁₆GaN**
(CH₃)₂HGa·N(CH₃)₃
Formation: 5.3.4.4.1
- C₅H₂₂B₆Si**
2-(Me₂Si)-μ-(Me₂B)-B₅H₇
Conversion to 6-CH₃-1-CB₅H₆: 5.3.2.7.6
- C₆AlF₉**
(CF₂=CF)₃Al
Formation: 5.3.3.4.4
- C₆BrF₅Mg**
C₆F₅MgBr
Formation: 5.4.2.2.1, 5.4.2.5.2
Reaction with R₂TiX: 5.3.6.3.1
- C₆CaF₅I**
C₆F₅CaI
Formation: 5.4.3.4.2
- C₆Cl₂F₅In**
C₆F₅InCl₂
Formation: 5.3.5.3.1
- C₆F₅I**
C₆F₅I
Reaction with In metal: 5.3.5.2.1
- C₆F₅I₂In**
C₆F₅InI₂
Formation: 5.3.5.2.1
- C₆F₅Li**
LiC₆F₅
Reaction with Ti(C₆F₅)₂Br: 5.3.6.3.1
- C₆F₉O₆Tl**
Tl(O₂CCF₃)₃
Preparation: 5.3.6.3.4
Thallating agent: 5.3.6.3.4
- C₆HF₅**
C₆F₅H
Reaction with RMgX: 5.4.2.5.2

- C₆H₄BClF₄N₂**
 [4-ClC₆H₄N₂][BF₄]
 Reaction with Tl metal: 5.3.6.2.5
- C₆H₄Br₂FIn**
 4-FC₆H₄InBr₂
 Formation: 5.3.5.3.4
- C₆H₄Br₂Mg₂**
 1,2-C₆H₄(MgBr)₂
 Formation: 5.4.2.3.1
- C₆H₄I₂**
 o-C₆H₄I₂
 Reaction with BI₃: 5.3.2.3.3
- C₆H₄Li₂**
 1,2-C₆H₄Li₂
 Reaction with MgX₂: 5.4.2.3.1
- C₆H₅AlCl₂**
 C₆H₅AlCl₂
 Reaction with [Ph₄C₄Li]₂: 5.3.3.3.1
- C₆H₅BBr₂**
 C₆H₅BBr₂
 Formation: 5.3.2.3.1
- C₆H₅BCl₂**
 C₆H₅BCl₂
 Cleavage of M—C: 5.3.2.3.1
 Formation: 5.3.2.3.1, 5.3.2.3.3
 Reaction with norbornadiene: 5.3.2.6.4
- C₆H₅BF₄N₂**
 [C₆H₅N₂][BF₄]
 Reaction with Tl metal: 5.3.6.2.5
- C₆H₅BI₂**
 C₆H₅BI₂
 Formation: 5.3.2.3.1, 5.3.2.3.3
 Reaction with h⁵-C₅H₅—M: 5.3.2.3.3
- C₆H₅BOS**
 1-C₆H₄SB(H)O
 Hydroborating agent: 5.3.2.5.1
- C₆H₅BO₂**
 2-C₆H₄OB(H)O
 Formation and hydroboration of alkenes: 5.3.2.5.1
- C₆H₅BrMg**
 C₆H₅MgBr
 Formation: 5.4.2.2.1
 Reaction with AlCl₃: 5.3.3.3.1
 Reaction with PbX₂: 5.4.7.2.5
 Reaction with R₃PbPbR₃: 5.4.7.2.2
- C₆H₅Br₂Ga**
 C₆H₅GaBr₂
 Formation: 5.3.4.3.5
- C₆H₅Br₂In**
 C₆H₅InBr₂
 Formation: 5.3.5.2.5, 5.3.5.3.4
- C₆H₅CaI**
 C₆H₅CaI
 Formation: 5.4.3.2.1
 Metallation of RH: 5.4.3.4.2
- C₆H₅ClMg**
 C₆H₅MgCl
 Reaction with PbX₂: 5.4.7.2.5
 Reaction with BeCl₂: 5.4.3.3.1
- C₆H₅Cl₂Ga**
 C₆H₅GaCl₂
 Formation: 5.3.4.3.5
 Molten, electrical conductor: 5.3.4.3.5
- C₆H₅Cl₂In**
 C₆H₅InCl₂
 Formation: 5.3.5.2.5, 5.3.5.3.4
- C₆H₅GaI₂**
 C₆H₅GaI₂
 Formation: 5.3.4.3.5
- C₆H₅I**
 C₆H₅I
 Reaction with Al metal: 5.3.3.2.2
- C₆H₅ISr**
 C₆H₅SrI
 Formation: 5.4.3.2.1
- C₆H₅I₂In**
 C₆H₅InI₂
 Formation: 5.3.5.3.4
- C₆H₅Li**
 LiC₆H₅
 Reaction with BeR₂: 5.4.3.4.4
- C₆H₅Na**
 Na[C₆H₅]
 Reaction with MgX₂: 5.4.2.3.1
- C₆H₆Be**
 (CH₃C≡C)₂Be
 Reaction with Me₂AlC≡CMe: 5.3.3.5.4
 Reaction with (AlR₃)₂: 5.4.3.4.4
- C₆H₅BeH**
 C₆H₅BeH
 Formation: 5.4.3.3.2
- C₆H₆F₆Sn**
 (CH₃)₂(CF=CF₂)₂Sn
 Reaction with BX₃: 5.3.2.3.1
- C₆H₆Hg**
 (CH₃C≡C)₂Hg
 Reaction with Al metal: 5.3.3.2.3
- C₆H₆Mg**
 (CH₃C≡C)₂Mg
 Reaction with Me₂AlC≡CMe: 5.3.3.5.4
- C₆H₅MgH**
 C₆H₅MgH
 Formation: 5.3.3.4.4, 5.4.2.4.3
- C₆H₇BCl₂**
 h¹-CH₃C₅H₄BCl₂
 Formation: 5.3.2.3.1

- C₆H₇BO₃**
3-HOC₆H₄B(OH)₂
Formation: 5.3.2.4.1
4-HOC₆H₄B(OH)₂
Formation: 5.3.2.4.1
- C₆H₈BLi**
LiC₆H₅BH₃
Formation: 5.3.2.5.2
- C₆H₈Be**
h⁵-C₅H₅BeCH₃
Formation: 5.4.3.3.1, 5.4.3.4.4
- C₆H₈IInN₂**
(CNCH₂CH₂)₂InI
Formation: 5.3.5.2.8
- C₆H₈IN₂TI**
(NCCH₂CH₂)₂TII
Formation: 5.3.6.2.9
- C₆H₈Mg₂**
C₆H₅Mg₂H₃
Formation: 5.4.2.4.3
- C₆H₈Zn₂**
C₆H₅Zn₂H₃
Formation: 5.3.3.4.4
- C₆H₉Al**
(CH₂=CH)₃Al
Decomposition: 5.3.3.2.3
Formation: 5.3.3.2.3
- C₆H₉BrMg**
CH₃(CH₂)₃C≡CMgBr
Formation: 5.4.2.5.2
- C₆H₉Ga**
(CH₂=CH)₃Ga
Formation: 5.3.4.2.3, 5.3.4.3.1
- C₆H₉O₆TI**
TI[OC(O)CH₃]₃
Reaction with olefins: 5.3.6.3.5
- C₆H₁₀**
C₂H₅C≡CC₂H₅
Reaction with BI₃: 5.3.2.3.4
- C₆H₁₀BI₃**
trans-C₂H₅(BI₂)C=CIC₂H₅
Formation: 5.3.2.3.4
- C₆H₁₀B₂**
2,3-(CH₃)₂C₄B₂H₄
Formation: 5.3.2.7.3
3,4-(CH₃)₂C₄B₂H₄
Formation: 5.3.2.7.3
- C₆H₁₀B₂Cl₄**
1,2-C₆H₁₀(BCl₂)₂
Formation: 5.3.2.3.4
- C₆H₁₀B₂I₂S**
C₆H₁₀B₂I₂S
Formation: 5.3.2.3.4
- C₆H₁₀Be**
(CH₃CH=CH)₂Be
Formation: 5.4.3.4.4
Oligomerization: 5.4.3.4.1
- C₆H₁₀CITI**
(CH₃CH=CH)₂TICl
Formation: 5.3.6.3.3
- C₆H₁₀Hg**
(cyclo-C₃H₅)₂Hg
Reaction with Al metal: 5.3.3.2.3
Reaction with BX₃: 5.3.2.3.1
- C₆H₁₁BrMg**
cyclo-C₆H₁₁MgBr
Reaction with R₃SCl: 5.4.4.2
- C₆H₁₁ClMg**
CH₂=C(CH₃)CH₂CH₂CH₂MgCl
Formation: 5.4.2.5.1
cyclo-C₆H₁₁MgCl
Reaction with R₃SnH: 5.4.6.5
- C₆H₁₂AlNa**
Na[(CH₃)₂AlC₄H₆]
Formation: 5.3.3.5.4
- C₆H₁₂BCl**
CH₂(CH₂)₅BCl
Formation: 5.3.2.5.1
C₂H₅CHC(C₂H₅)BHCl
Formation: 5.3.2.5.1
- C₆H₁₂Br₂Mg₂O**
O(CH₂CH₂CH₂MgBr)₂
Formation: 5.4.2.2.1
- C₆H₁₂Mg**
CH₂(CH₂)₅Mg
Formation: 5.4.2.3.2
- C₆H₁₂Si**
CH₂CH=CHCH₂Si(CH₃)₂
Formation: 5.4.2.2.4
- C₆H₁₃B**
CH₂(CH₂)₃BC₂H₅
Formation: 5.3.2.5.1, 5.3.2.6.1
CH₂(CH₂)₅BH
Formation: 5.3.2.5.1
H₃CCHCH(BH₂)CH₂CH₂CH₂
Formation: 5.3.2.5.1
- C₆H₁₃BCl₂**
CH₃(CH₂)₅BCl₂
Formation: 5.3.2.5.1
C₂H₅CH(n-C₃H₇)BCl₂
Formation: 5.3.2.5.1
- C₆H₁₃BO₂**
CH₃(CH₂)₃CHCHB(OH)₂
Formation: 5.3.2.5.1

- $\text{OCH}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{OBH}$
 Hydroborating agent: 5.3.2.5.1
- $\text{C}_6\text{H}_{13}\text{BaIO}$**
 $\text{C}_2\text{H}_5\text{IBa} \cdot \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$
 Formation: 5.4.3.2.1
- $\text{C}_6\text{H}_{13}\text{FMg}$**
 $n\text{-C}_6\text{H}_{13}\text{MgF}$
 Formation: 5.4.2.2.1
- $\text{C}_6\text{H}_{13}\text{O}_2\text{Ti}$**
 $(\text{CH}_3)_2\text{Ti}[\text{OC}(\text{O})\text{CH}(\text{CH}_3)_2]$
 Formation: 5.3.6.3.8
- $\text{C}_6\text{H}_{14}\text{BCl}$**
 $(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{BHCl}$
 Hydroborating agent: 5.3.2.5.1
- $\text{C}_6\text{H}_{14}\text{Be}$**
 $[(\text{CH}_3)_2\text{CH}]_2\text{Be}$
 Formation: 5.4.3.3.1
 $(n\text{-C}_3\text{H}_7)_2\text{Be}$
 Formation: 5.4.3.3.1, 5.4.3.4.4
- $\text{C}_6\text{H}_{14}\text{Ga}_2\text{I}_4$**
 $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}_2\text{I}_4$
 Formation: 5.3.4.2.1
- $\text{C}_6\text{H}_{14}\text{Hg}$**
 $(i\text{-C}_3\text{H}_7)_2\text{Hg}$
 Reaction with Al metal: 5.3.3.2.3
- $\text{C}_6\text{H}_{14}\text{Mg}$**
 $(i\text{-C}_3\text{H}_7)_2\text{Mg}$
 Formation: 5.4.2.3.2
 Reaction with alkynes: 5.4.2.5.2
 Redistribution with MgH_2 : 5.4.2.4.3
 $(n\text{-C}_3\text{H}_7)_2\text{Mg}$
 Formation: 5.4.2.4.1
- $\text{C}_6\text{H}_{14}\text{MgO}_4$**
 $\text{Mg}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)\text{OCH}_3$
 Catalyst in RMgX formation: 5.4.2.2.1
- $\text{C}_6\text{H}_{15}\text{Al}$**
 $(\text{C}_2\text{H}_5)_3\text{Al}$
 Aluminination of alkynes: 5.3.3.5.2
 Catalyst for MgH_2 addition to olefins: 5.4.2.4.1
 Electrolysis at a Ga metal anode: 5.3.4.2.4
 Exchange with R_3B : 5.3.3.5.4
 Exchange with $\text{M}[\text{R}_4\text{B}]$: 5.3.3.5.4
 Exchange with R_3B : 5.3.3.5.4
 Exchange with R_4Sb : 5.3.3.5.4
 Formation: 5.3.3.2.1, 5.3.3.2.3, 5.3.3.3.3, 5.3.3.4.2, 5.3.3.4.4
 Photochemical reaction with diphenylacetylene: 5.3.3.5.4
 Pyrolysis: 5.3.3.5.3
 Reaction at an In metal anode: 5.3.5.2.7
- Reaction with $\text{Li}[\text{AlH}_4]$: 5.3.3.4.3
 Reaction with $\text{Na}[\text{AlH}_4]$: 5.3.3.4.3
 Reaction with $\text{R}_3\text{Al}_2\text{Cl}_3$: 5.3.3.3.2
 Reaction with BX_3 : 5.3.2.3.1
 Reaction with GaX_3 : 5.3.4.3.1
 Reaction with GeX_4 : 5.3.13.5
 Reaction with R_3SnLi : 5.3.18.3
 Reaction with CH_2N_2 : 5.3.3.5.5
 Reaction with KC_6H_6 in THF: 5.3.3.5.4
 Reaction with C_2H_4 : 5.3.3.5.1
 Reaction with alkenes: 5.3.3.5.1
 $(n\text{-C}_3\text{H}_7)_2\text{AlH}$
 Formation: 5.3.3.2.1
- $\text{C}_6\text{H}_{15}\text{AlNaO}_4$**
 $\text{Na}[\text{AlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$
 Catalyst in RMgX formation: 5.4.2.2.1
- $\text{C}_6\text{H}_{15}\text{Al}_2\text{Br}_3$**
 $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Br}_3$
 Formation: 5.3.3.2.2
- $\text{C}_6\text{H}_{15}\text{Al}_2\text{Cl}_3$**
 $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$
 Formation: 5.3.3.2.2
 Reaction with KCl : 5.3.3.3.2
 Reaction with NaH : 5.3.3.3.3
- $\text{C}_6\text{H}_{15}\text{Al}_2\text{I}_3$**
 $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{I}_3$
 Formation: 5.3.3.2.2
- $\text{C}_6\text{H}_{15}\text{B}$**
 $(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{BH}_2$
 Formation: 5.3.2.5.1, 5.3.2.6.1
 Hydroboration of alkenes: 5.3.2.5.1
 Hydroboration of alkynes: 5.3.2.5.1
 Reactivity toward functional groups: 5.3.2.5.1
 $(\text{C}_2\text{H}_5)_3\text{B}$
 Catalyst for polymerization of C_2H_4 by MgH_2 : 5.4.2.4.1
 Formation: 5.3.2.3.1, 5.3.2.4.3, 5.3.2.6.1, 5.3.3.5.4, 5.4.3.4.4
 Reaction with diborane: 5.3.2.5.3
 Redistribution with BCl_3 : 5.3.2.3.6
- $\text{C}_6\text{H}_{15}\text{BCIN}$**
 $(\text{CH}_3)_2\text{NB}(n\text{-C}_4\text{H}_9)\text{Cl}$
 Reactions with R_3SiK : 5.3.7.4.1
- $\text{C}_6\text{H}_{15}\text{BF}_4\text{O}$**
 $[(\text{C}_2\text{H}_5)_3\text{O}]\text{BF}_4$
 Reaction with $\text{B}_{10}\text{H}_{13}\text{MgI}$: 5.3.2.7.6
- $\text{C}_6\text{H}_{15}\text{BN}_2\text{Sn}$**
 $(\text{CH}_3)_3\text{SnBN}(\text{CH}_2)_3\text{N}$
 Formation: 5.3.17.2.2

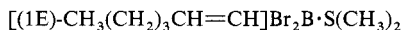
- C₆H₁₅BO₃**
 (C₂H₅O)₃B
 Reaction with R₂Zn: 5.3.2.4.3
- C₆H₁₅BeLiN**
 LiBe[C(CH₃)₃]·N(CH₃)₂
 Formation: 5.4.3.3.1
- C₆H₁₅BrPb**
 (C₂H₅)₃PbBr
 Reaction with Mg metal: 5.4.7.2.4
- C₆H₁₅Br₃Ga₂**
 (CH₃CH₂)₃Ga₂Br₃
 Formation: 5.3.4.2.1
- C₆H₁₅Br₃In₂**
 (CH₃CH₂)₃In₂Br₃
 Formation: 5.3.5.2.1
- C₆H₁₅ClMgPb**
 (C₂H₅)₃PbMgCl
 Formation: 5.4.7.2.5
- C₆H₁₅ClSi**
 (C₂H₅)₃SiCl
 Reaction with LiB₅H₈: 5.3.7.3.2
- C₆H₁₅Ga**
 (C₂H₅)₃Ga
 Formation: 5.3.4.2.2, 5.3.4.2.3, 5.3.4.3.1,
 5.3.4.4.1, 5.3.4.5.2
 Reaction with alkynes: 5.3.4.5.1
 Reaction with cyanide anion: 5.3.4.5.3
 Reaction with potassium metal: 5.3.4.5.4
- C₆H₁₅Ga₂I₃**
 (CH₃CH₂)₃Ga₂I₃
 Formation: 5.3.4.2.1
- C₆H₁₅I₃In₂**
 (CH₃CH₂)₃In₂I₃
 Formation: 5.3.5.2.1
- C₆H₁₅In**
 (C₂H₅)₃In
 Formation: 5.3.5.2.3, 5.3.5.2.7, 5.3.5.3.1
 Reaction with InX₃: 5.3.5.3.2
- C₆H₁₅LiSn**
 (C₂H₅)₃SnLi
 Reaction with (R₂N)₂BX and R₂NBX₂:
 5.3.17.2.2
- C₆H₁₅Tl**
 (C₂H₅)₃Tl
 Formation: 5.3.6.2.1, 5.3.6.3.2
 Reaction with R₃GeH and (Me₃Si)^{*}
 CH₂)₃GeH: 5.3.16
 Reaction with R₃SiH: 5.3.11.1
 Reaction with (Me₃SiCH₂)₃SnH: 5.3.21.1
 Reaction with R₃SnH: 5.3.21.1
- C₆H₁₆AlNa**
 Na[(C₂H₅)₃AlH]
 Formation: 5.3.3.4.3
- Reaction with alkynes: 5.3.3.5.2
- C₆H₁₆BNa**
 Na[(C₂H₅)₃BH]
 Reaction with BeR₂ and BeX₂: 5.4.3.3.2
 Reaction with RBeX: 5.4.3.4.3
- C₆H₁₆B₂O₄**
 (HO)₂B(CH₂)₆B(OH)₂
 Formation: 5.3.2.4.1
- C₆H₁₆Be₂**
 Be₂H(C₂H₅)₃
 Formation: 5.4.3.4.4
- C₆H₁₆Ge**
 (C₂H₅)₃GeH
 Reaction with TIR₃: 5.3.16
- C₆H₁₆Si**
 (C₂H₅)₃SiH
 Reaction with TIR₃: 5.3.11.1
- C₆H₁₆Sn**
 (C₂H₅)₃SnH
 Reaction with Tl(GeR₃)₃ and TIR₃:
 5.3.21.1
 Reaction with BeR₂: 5.4.3.4.3
- C₆H₁₈AlLiSn**
 Li[(CH₃)₃SnAl(CH₃)₃]
 Formation: 5.3.18.3
- C₆H₁₈AlN**
 (CH₃)₃Al·N(CH₃)₃
 Reaction with H₃Al·NR₃: 5.3.3.4.3
- C₆H₁₈Al₂**
 [(CH₃)₃Al]₂
 Effect on reaction of MgH₂ with C₂H₄:
 5.4.2.4.1
 Reaction with BeR₂: 5.4.3.4.4
- C₆H₁₈BN₃**
 B[N(CH₃)₂]₃
 Formation: 5.3.7.3.1
 Reaction with R₃B: 5.3.2.6.1
- C₆H₁₈B₂**
 (C₂H₅)₂BH₂BHC₂H₅
 Formation: 5.3.2.5.3
- C₆H₁₈B₁₀**
 6-C₆H₅B₁₀H₁₃
 Formation: 5.3.2.7.6
- C₆H₁₈ClSi₂Tl**
 ClTi[Si(CH₃)₃]₂
 Formation: 5.3.11.2
- C₆H₁₈GaLiSn**
 Li[(CH₃)₃SnGa(CH₃)₃]
 Formation: 5.3.4.5.4, 5.3.19
- C₆H₁₈GaN**
 (CH₃)₃Ga·N(CH₃)₃
 Reaction with Me₃N·GaH₃: 5.3.4.4.1

- Reaction with LiH: 5.3.4.4.1
- C₆H₁₈Ga₂K₂**
 $K_2[(CH_3)_3GaGa(CH_3)_3]$
 Formation: 5.3.4.5.4
- C₆H₁₈Ge₂Hg**
 $[(CH_3)_3Ge]_2Hg$
 Reaction with Al metal: 5.3.13.2
 Reaction with Mg metal: 5.4.5.5
- C₆H₁₈HgSi₂**
 $[(CH_3)_3Si]_2Hg$
 Reaction with Mg: 5.4.4.4
 Reaction with Al metal: 5.3.8.3
 Reaction with TiR₃: 5.3.11.2
 Reaction with Ga metal: 5.3.9
 Reaction with Na or K and (R₃Si)₃Al*
 OEt₂: 5.3.8.5
- C₆H₁₈HgSn₂**
 $[(CH_3)_3Sn]_2Hg$
 Reaction with Al metal: 5.3.18.2
- C₆H₁₈InLiSn**
 $Li[(CH_3)_3SnIn(CH_3)_3]$
 Formation: 5.3.20
- C₆H₁₈LiSnTi**
 $Li[(CH_3)_3SnTi(CH_3)_3]$
 Formation: 5.3.21.2, 5.3.21.3
- C₆H₁₈N₃OP**
 $OP[N(CH_3)_2]_3$
 Solvent: 5.4.2.2.1
- C₆H₁₈OSi₂**
 $(CH_3)_3SiOSi(CH_3)_3$
 Reaction with GaX₃: 5.3.4.3.2
- C₆H₁₈Si₂**
 $(CH_3)_3SiSi(CH_3)_3$
 Formation: 5.3.7.3.1
- C₆H₁₈Sn₂**
 $(CH_3)_3SnSn(CH_3)_3$
 Reaction with Li[GaR₄]: 5.3.4.5.4
 Reaction with Li[R₄Tl]: 5.3.21.3
 Reaction with RMgX: 5.4.6.4
- C₆H₂₀BeN₂**
 $BeH_2 \cdot 2 N(CH_3)_3$
 Reaction with olefins: 5.4.3.4.3
- C₆H₂₁B₉BeO**
 $3-Be[O(C_2H_5)_2] \cdot 1,2-B_9C_2H_{11}$
 Formation: 5.4.3.4.2
- C₆H₂₁Ge₃O₃**
 $[(CH_3)_2GeOH]_3$
 Formation: 5.3.4.3.1
- C₆H₂₂B₁₀N₂**
 $(C_2H_5NC)_2B_{10}H_{12}$
 Formation: 5.3.2.7.4
- C₇H₅ClO**
 C_6H_5COCl
 Reaction with $[B_{10}H_{10}]^{2-}$: 5.3.2.7.6
- C₇H₅F₃**
 $C_6H_5CF_3$
 Reaction with $Tl(O_2CCF_3)_3$: 5.3.6.3.4
- C₇H₆O₂**
 $C_6H_5CO_2H$
 Reaction with $Tl(O_2CCF_3)_3$: 5.3.6.3.4
- C₇H₇BF₄N₂**
 $[4-CH_3C_6H_4N_2][BF_4]$
 Reaction with Tl metal: 5.3.6.2.5
- C₇H₇BF₄N₂O**
 $[2-CH_3OC_6H_4N_2][BF_4]$
 Reaction with Tl metal: 5.3.6.2.5
 $[4-CH_3OC_6H_4N_2][BF_4]$
 Reaction with Tl metal: 5.3.6.2.5
- C₇H₇BrMg**
 $4-CH_3C_6H_4MgBr$
 Reaction with alkynes: 5.4.2.5.1
- C₇H₇Br₂In**
 $4-CH_3C_6H_4InBr_2$
 Formation: 5.3.5.3.4
- C₇H₇CaIO**
 $o-CH_3OC_6H_4CaI$
 Formation: 5.4.3.4.2
- C₇H₇ClMg**
 $C_6H_5CH_2MgCl$
 Reaction with R₃GeD and α-NpPhMe*
 GeH: 5.4.5.3
 Reaction with olefins: 5.4.2.5.1
- C₇H₇Cl₂Tl**
 $C_6H_5(ClCH_2)TlCl$
 Formation: 5.3.6.3.6
- C₇H₇I**
 $p-CH_3C_6H_4I$
 Reaction with Al metal: 5.3.3.2.2
- C₇H₇ISr**
 $CH_3C_6H_4SrI$
 Formation: 5.4.3.2.1
- C₇H₈BBr**
 $CH_3(C_6H_5)BBr$
 Formation: 5.3.2.3.1
- C₇H₈Be**
 $(o-C_6H_4CH_3)BeH$
 Formation: 5.4.3.3.2
- C₇H₈O**
 $C_6H_5OCH_3$
 Reaction with $Tl(O_2CCF_3)_3$: 5.3.6.3.4
 Reaction with RMgX: 5.4.2.5.2
- C₇H₉BO₂**
 $C_6H_5CH_2B(OH)_2$
 Formation: 5.3.2.4.1
 $4-CH_3C_6H_4B(OH)_2$
 Reaction with RTiCl₂: 5.3.6.3.3

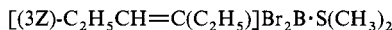
- C₇H₅ClMg**
2-chloromagnesonortricyclene
Formation: 5.4.2.2.1
- C₇H₁₀Be**
h⁵-C₅H₅BeC₂H₅
Formation: 5.4.3.4.4
- C₇H₁₁BeN**
h⁵-C₅H₅BeN(CH₃)₂
Formation: 5.4.3.3.2
- C₇H₁₁ClMg**
 $\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{C}(\text{CH}_3)\text{MgCl}}$
Formation: 5.4.2.2.1
 $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$
Rearrangement: 5.4.2.2.1
- C₇H₁₁Ga**
(CH₃)₂GaC₅H₅-h¹
Formation: 5.3.4.3.1
- C₇H₁₁In**
(CH₃)₂InC₅H₅-h¹
Formation: 5.3.5.4.2
- C₇H₁₁Tl**
(CH₃)₂TlC₅H₅
Formation: 5.3.6.4.1
- C₇H₁₂Br₂Mg₂O**
 $\text{CH}_3(\text{BrMg})\text{C}=\text{C}[\text{CHMe}_2]\text{CH}_2\text{OMgBr}$
Formation: 5.4.2.5.1
- C₇H₁₂Si**
(CH₃)₃SiC≡CCH=CH₂
Reaction with RCaX, RBaX: 5.4.3.4.1
- C₇H₁₃Al**
(CH₃)₃AlC≡CC₃H₇-n
Reaction with (h⁵-C₅H₅)₂ZrMeCl:
5.3.3.5.1
- C₇H₁₃ClMg**
 $\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CHCH}_2\text{MgCl}}$
Formation: 5.4.2.2.1
 $\text{CH}_3\text{CH}(\text{MgCl})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
Rearrangement: 5.4.2.2.1
- C₇H₁₃ClMgO₂**
 $\overline{\text{OCH}_2\text{CH}_2\text{OC}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl})}$
Formation: 5.4.2.2.1
- C₇H₁₄BBr₂ClS**
[(1E)-ClCH₂(CH₂)₂CH=CH]Br₂B·S(C*H₃)₂
Formation: 5.3.2.5.1
- C₇H₁₅AlO**
 $\overline{\text{i-C}_4\text{H}_9\text{AlCH}_2\text{CH}_2\text{CH}_2\text{O}}$
Formation: 5.3.3.4.2
- C₇H₁₅BO**
 $\overline{\text{CH}_2(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{BOCH}_3}$
Formation: 5.3.2.6.2
- $\overline{\text{CH}_2(\text{CH}_2)_3\text{BOCH}_3}$
Formation: 5.3.2.6.2
- C₇H₁₅BO₂**
 $\overline{\text{CH}_2(\text{CH}_2)_2\text{OBO}(\text{CH}_2)_3\text{CH}_3}$
Formation: 5.3.2.5.1
- C₇H₁₅B₅**
2-C₆H₅CH₂-B₅H₈
Formation: 5.3.2.7.6
- C₇H₁₅CaI**
C₇H₁₅CaI
Formation: 5.4.3.2.1
- C₇H₁₅Cl₂Ga**
n-C₇H₁₅GaCl₂
Formation: 5.3.4.4.1
- C₇H₁₅O₂Tl**
CH₃(C₂H₅)₂Tl[OC(O)CH(CH₃)₂]
Formation: 5.3.6.3.8
- C₇H₁₇AlO**
(CH₃)₃Al·OC₄H₈
Reaction with NaC₄H₆ in THF:
5.3.3.5.4
- C₇H₁₇ClMgOSi**
(CH₃)₃SiOCH₂CH₂CH₂CH₂MgCl
Formation: 5.4.2.2.1
- C₇H₁₇ClOSi**
(CH₃)₃SiOCH₂CH₂CH₂CH₂Cl
Reaction with Mg metal: 5.4.2.2.1
- C₇H₁₉AlO**
(CH₃)₃Al·O(C₂H₅)₂
Reaction with Me₂Si(N=PMe₃)₂:
5.3.3.5.4
- C₇H₁₉AlSn**
(CH₃)₃SnAl(C₂H₅)₂
Formation: 5.3.18.3
- C₇H₁₉BClNSn**
(CH₃)₃SnBClN(C₂H₅)₂
Formation: 5.3.17.2.2
- C₇H₁₉BN₂Pb**
 $\overline{(\text{CH}_3)_3\text{PbB}(\text{CH}_3)\text{N}(\text{CH}_2)_2\text{NCH}_3}$
Formation: 5.3.22.2
- C₇H₁₉B₃O₆**
CH[B(OCH₃)₂]₃
Formation: 5.3.2.3.2
- C₇H₁₉BrMgN₂**
CH₃MgBr[(CH₃)₂NCH₂CH₂N(CH₃)₂]
Formation: 5.4.2.3.2
- C₇H₁₉GaO**
(CH₃)₃Ga·O(C₂H₅)₂
Formation: 5.3.4.2.2
- C₇H₁₉GaS**
(CH₃)₃Ga·S(C₂H₅)₂
Formation: 5.3.4.2.2

- C₇H₁₉InO**
 (CH₃)₃In·O(C₂H₅)₂
 Formation: 5.3.5.2.3
- C₇H₁₉LiSi₂**
 [(CH₃)₃Si]₂CHLi
 Reaction with AlCl₃: 5.3.3.3.1
 Reaction with GaX₃: 5.3.4.3.1
 Reaction with InX₃: 5.3.5.3.1
- C₇H₂₀AlN**
 H(C₂H₅)₂Al·N(CH₃)₃
 Formation: 5.3.3.4.3
- C₇H₂₀B₄Ge**
 (CH₃)₃Ge(CH₃)₂C₂B₄H₅
 Formation: 5.3.12.3
 Isomerization: 5.3.12.3
- C₇H₂₀B₄Si**
 μ-(CH₃)₃Si(CH₃C)₂B₄H₅
 Formation: 5.3.7.3.2
- C₇H₂₀B₁₀**
 6-C₆H₅CH₂B₁₀H₁₃
 Formation: 5.3.2.7.6
- C₇H₂₀InP**
 (CH₃)₃PCH₂In(CH₃)₃
 Formation: 5.3.5.4.2
- C₇H₂₁BN₂Si**
 (CH₃)₃SiB[N(CH₃)₂]₂
 Formation: 5.3.7.3.1
 Pyrophoric: 5.3.7.3.1
- C₇H₃₃B₁₈N**
 [C₆H₁₁NH₂]⁺[nido-CB₁₈H₂₀]⁻
 Formation: 5.3.2.7.4
- C₈F₁₁O₆S₂Tl**
 C₆F₅Tl(O₃SCF₃)₂
 Formation: 5.3.6.3.4
- C₈HF₁₀O₆S₂Tl**
 3-C₆HF₄Tl(O₃SCF₃)₂
 Formation: 5.3.6.3.4
- C₈H₂F₉O₆S₂Tl**
 3,5-C₆H₂F₃Tl(O₃SCF₃)₂
 Formation: 5.3.6.3.4
- C₈H₃B₂I₄MnO₃**
 h⁵-C₅H₃-1,3-(BI₂)₂Mn(CO)₃
 Formation: 5.3.2.3.3
- C₈H₄BBr₂MnO₃**
 h⁵-C₅H₄BBr₂Mn(CO)₃
 Formation: 5.3.2.3.3
- C₈H₄BI₂MnO₃**
 h⁵-C₅H₄BI₂Mn(CO)₃
 Formation: 5.3.2.3.3
- C₈H₄BaHg**
 BaHg(C≡CH)₄
 Formation: 5.4.3.3.1
- C₈H₅B₂CoLi**
 Li[h⁵-C₅H₅CoC₂B₂C]
 Reaction with SnCl₂: 5.3.17.3.3
- C₈H₅CaI**
 (C₆H₅C≡C)CaI
 Formation: 5.4.3.4.2
- C₈H₅Li**
 LiC≡CC₆H₅
 Reaction with BeR₂: 5.4.3.4.4
- C₈H₅MnO₃**
 h⁵-C₅H₅Mn(CO)₃
 Reaction with BX₃: 5.3.2.3.3
- C₈H₆**
 C₆H₅C≡CH
 Reaction with BX₃: 5.3.2.3.4
- C₈H₆BBr₃**
 C₆H₅(Br)C=CHBBr₂
 Mixed isomer formation: 5.3.2.3.4
- C₈H₆BCl₃**
 C₆H₅(Cl)C=CHBCl₂
 Mixed isomer formation: 5.3.2.3.4
- C₈H₆BI₃**
 C₆H₅(I)C=CHBI₂
 Mixed isomer formation: 5.3.2.3.4
- C₈H₇BrMg**
 C₆H₅CH=CHMgBr
 Formation: 5.4.2.2.1
- C₈H₇ClMg**
 CH₂=C(C₆H₅)MgCl
 Reaction with B(OR)₃: 5.3.2.4.1
- C₈H₇N**
 C₆H₅CH₂CN
 Reaction with Mg: 5.4.2.2.5
- C₈H₈**
 C₆H₅CH=CH₂
 Reaction with R₂AlH: 5.3.3.4.1
 Reaction with Mg metal: 5.4.2.2.4
- C₈H₈K₂**
 K₂[cyclo-C₈H₈]
 Formation: 5.4.2.3.1
 Reaction with MgBr₂: 5.4.2.3.1
- C₈H₈Mg**
 Mg[cyclo-C₈H₈]
 Formation: 5.4.2.3.3, 5.4.2.2.4
 Reaction with H₂O: 5.4.2.2.4
 o-C₆H₄MgCH₂CH₂
 Formation: 5.4.2.2.1
- C₈H₉BF₄N₂**
 [4-C₂H₅C₆H₄N₂][BF₄]
 Reaction with Tl metal: 5.3.6.2.5
- C₈H₉BF₄N₂O**
 [4-C₂H₅OC₆H₄N₂][BF₄]
 Reaction with Tl metal: 5.3.6.2.5

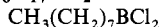
- C₈H₉BrMg**
 $\text{C}_6\text{H}_5\text{CH}(\text{MgBr})\text{CH}_3$
 Formation: 5.4.2.5.3
- C₈H₉Cl₂Tl**
 $4\text{-CH}_3\text{C}_6\text{H}_4(\text{ClCH}_2)\text{TlCl}$
 Formation: 5.3.6.3.6
- C₈H₁₀BrMgN**
 $4\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{MgBr}$
 Formation: 5.4.2.2.1
- C₈H₁₀IMgN**
 $p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{MgI}$
 Formation: 5.4.2.3.1
- C₈H₁₀LiN**
 $p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{Li}$
 Reaction with MgX_2 : 5.4.2.3.1
- C₈H₁₀O**
 $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$
 Reaction with $\text{Tl}(\text{O}_2\text{CCF}_3)_3$: 5.3.6.3.4
- C₈H₁₁Al**
 $(\text{CH}_3)_2\text{AlC}_6\text{H}_5$
 Formation: 5.3.3.5.4
- C₈H₁₁Li**
 $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Li}$
 Reaction with R_2AlCl or R_3Al : 5.3.8.2.1
- C₈H₁₁LiSi**
 $\text{Li}[(\text{CH}_3)_2\text{SiC}_6\text{H}_5]$
 Reaction with RMgX : 5.4.4.7
- C₈H₁₁N**
 $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$
 Catalyst for reaction of Ga metal with
 RX: 5.3.4.2.2
- C₈H₁₂**
 $\text{C}_6\text{H}_9\text{CHCH}_2$
 Reaction with LiAlH_4 : 5.3.3.4.1
- C₈H₁₂AlLi**
 $\text{Li}[(\text{CH}_2=\text{CH})_4\text{Al}]$
 Formation: 5.3.3.4.4
 $\text{Li}[(\text{CH}_3)_2(\text{CH}_3\text{C}\equiv\text{C})_2\text{Al}]$
 Formation: 5.3.3.5.4
- C₈H₁₂B₂F₂**
 $\text{FBC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{B}(\text{F})\text{C}(\text{CH}_3)\text{CCH}_3$
 Formation: 5.3.2.3.4
- C₈H₁₂B₈FeSn**
 $\text{SnFe}[(\text{CH}_3)_2\text{C}_2\text{B}_4]_2$
 Formation: 5.3.17.3.2
- C₈H₁₂Cl₂Mg₂**
 $\text{ClMgCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CHC}^*$
 H_2MgCl
 Formation from MgCl_2 : 5.4.2.3.1
- C₈H₁₂Mg**
 $\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{Mg}$
 Formation: 5.4.2.2.4
- C₈H₁₂Na₂**
 $\text{Na}[\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}^*\text{CH}_2]\text{Na}$
 Reaction with MgX_2 : 5.4.2.3.1
- C₈H₁₂Sn**
 $(\text{CH}_2=\text{CH})_4\text{Sn}$
 Reaction with BX_3 : 5.3.2.3.1
- C₈H₁₄AlGeLi**
 $\text{Li}[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{GeAlH}_3]$
 Formation: 5.3.13.4
- C₈H₁₄BrInO₄**
 $\text{BrIn}(\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)_2$
 Formation: 5.3.5.2.2
- C₈H₁₄Hg**
 $(\text{CH}_2=\text{CHCH}_2\text{CH}_2)_2\text{Hg}$
 Reaction with Al metal: 5.3.3.2.3
- C₈H₁₅B**
 9-HB-bicyclo[3.3.1] C_8H_{14}
 Hydroboration of allenes: 5.3.2.5.1
 Hydroboration reagent: 5.3.2.5.1
 Isomerization: 5.3.2.6.2
 Reactivity toward functional groups:
 5.3.2.5.1
- C₈H₁₅Li**
 $\text{LiCH}_2\text{CH}=\text{CHCH}_2\text{C}(\text{CH}_3)_3$
 Reaction with MgX_2 : 5.4.2.3.1
- C₈H₁₅NSi**
 $\text{CHCHCHN}(\text{CH}_3)\text{CSi}(\text{CH}_3)_3$
 Reaction with BX_3 : 5.3.2.3.1
- C₈H₁₆B₄**
 $(\text{CH}_3)_4\text{C}_4\text{B}_4\text{H}_4$
 Formation: 5.3.2.7.3
- C₈H₁₆Li**
 $\text{Li}\{9\text{-H}_2\text{B-bicyclo}[3.3.1]\text{C}_8\text{H}_{14}\}$
 Formation: 5.3.2.5.2
- C₈H₁₆SiSn**
 $(\text{CH}_3)_2\text{SiCH}=\text{CHSn}(\text{CH}_3)_2\text{CH}=\text{CH}$
 Reaction with RBX_2 : 5.3.2.3.1
- C₈H₁₇B**
 $\text{CH}_2(\text{CH}_2)_3\text{BC}(\text{CH}_3)_3$
 Formation: 5.3.2.5.1
 $\text{CH}_3\text{B}(\text{CH}_2)_4\text{CHC}_2\text{H}_5$
 Formation: 5.3.2.6.3
 $n\text{-C}_4\text{H}_9\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$
 Formation: 5.3.2.6.3
 $s\text{-C}_4\text{H}_9\text{BCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$
 Formation: 5.3.2.6.3

C₈H₁₇BBr₂S

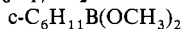
Formation: 5.3.2.5.1



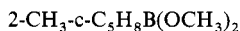
Formation: 5.3.2.5.1

C₈H₁₇BCl₂

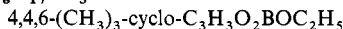
Formation: 5.3.2.5.1

C₈H₁₇BO₂

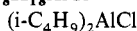
Formation: 5.3.2.5.1



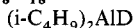
Formation: 5.3.2.5.1

C₈H₁₇BO₃Reaction with CH₂=C=CHMgBr:
5.3.2.4**C₈H₁₇O₂Tl**

Formation: 5.3.6.3.8

C₈H₁₈AlCl

Thermal decomposition: 5.3.3.3.2

Reaction with K[SiH₃]: 5.3.8.2.1**C₈H₁₈AlD**

Reaction with 1,1-dimethylindene, stereochemistry: 5.3.3.4.1

C₈H₁₈BBr

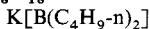
Formation: 5.3.2.5.1

C₈H₁₈BCl

Formation: 5.3.2.5.1



Formation: 5.3.2.5.1

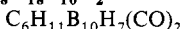
C₈H₁₈BK

Constitution: 5.3.2.3.2

Formation: 5.3.2.3.2

C₈H₁₈B₂

Formation: 5.3.2.5.1

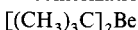
C₈H₁₈B₁₀O₂

Formation: 5.3.2.7.5

C₈H₁₈Be

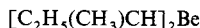
Formation: 5.4.3.3.1, 5.4.3.4.4

Isomerization: 5.4.3.4.3

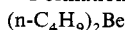


Formation: 5.4.3.3.1

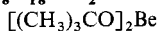
Isomerization: 5.4.3.4.3

Reaction with BeCl₂: 5.4.3.3.2Redistribution with BeR₂: 5.4.3.4.4

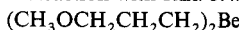
Formation: 5.4.3.3.1



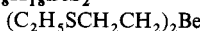
Formation: 5.4.3.3.1

C₈H₁₈BeO₂

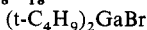
Reaction with RLi: 5.4.3.3.1



Formation: 5.4.3.3.1

C₈H₁₈BeS₂

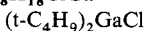
Formation: 5.4.3.3.1

C₈H₁₈BrGa

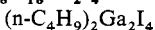
Formation: 5.3.4.3.5

C₈H₁₈Ca

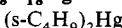
Polymerization of dienes: 5.4.3.4.1

C₈H₁₈ClGa

Formation: 5.3.4.3.5

C₈H₁₈Ga₂I₄

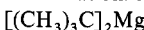
Formation: 5.3.4.2.1

C₈H₁₈Hg

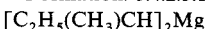
Reaction with Al metal: 5.3.3.2.3

C₈H₁₈Mg

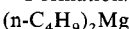
Formation: 5.4.2.3.1, 5.4.2.3.2



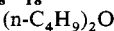
Formation: 5.4.2.3.1, 5.4.2.3.2



Formation: 5.4.2.3.1, 5.4.2.4.1



Formation: 5.4.2.3.1, 5.4.2.3.2

Redistribution with MgX₂: 5.4.2.3.2**C₈H₁₈O**Catalyst for reaction of Ga metal with
RX: 5.3.4.2.2**C₈H₁₈Si**Reaction with R₂AlH: 5.3.3.4.1**C₈H₁₈Zn**Reaction with Ca, Sr and Ba metals:
5.4.3.2.2

C₈H₁₉Al(i-C₄H₉)₂AlH

Bis-hydroalumination: 5.3.3.4.1

cis-hydroalumination: 5.3.3.4.1

Formation: 5.3.3.2.1

Hydroalumination of nonconjugated
polyenes: 5.3.3.5.1

Hydroalumination reagent: 5.3.3.4.1

Metallation of alkynes: 5.3.3.5.2

Rate of hydroalumination of cycloole-
fins: 5.3.3.4.1

Reaction with HCN: 5.3.3.5.2

Reaction with H₂C=CHCH₂OH:
5.3.3.4.2

Reaction with dienes: 5.3.3.5.1

Reaction with non-terminal alkynes, re-
giospecificity: 5.3.3.4.1

Reaction with styrene: 5.3.3.4.1

Reaction with vinylsilanes: 5.3.3.4.1

Reaction with 1-alkynylsilanes, solvent
influence: 5.3.3.4.1(n-C₄H₉)₂AlH

Formation: 5.3.3.2.1

C₈H₁₉AlO(C₂H₅)₂AlOC₄H₉-n

Formation: 5.3.3.4.3

C₈H₁₉BBr₂S[C₂H₅CH(n-C₃H₇)]Br₂B·S(CH₃)₂

Formation: 5.3.2.5.1

C₈H₁₉BO₂n-C₃H₇CH(CH₃)CH₂B(OCH₃)₂

Formation: 5.3.2.5.1

n-C₃H₇CH(C₂H₅)B(OCH₃)₂

Formation: 5.3.2.5.1

C₈H₁₉Ga(i-C₄H₉)₂GaH

Elimination of isobutylene: 5.3.4.4.2

Formation: 5.3.4.4.2

C₈H₂₀AlCaCa[Al(C₂H₅)₄]

Formation: 5.4.3.2.2

C₈H₂₀AlNaNa[(C₂H₅)₄Al]Exchange with R₃B: 5.3.3.5.4Reaction with Na[AlH₄]: 5.3.3.4.3Reaction with MX₂: 5.4.3.3.1Reaction with R₃Al: 5.3.3.5.4

Reaction with benzene: 5.3.3.5.2

C₈H₂₀AlSrSr[Al(C₂H₅)₄]

Formation: 5.4.3.2.2

C₈H₂₀BBaBa[B(C₂H₅)₄]

Formation: 5.4.3.2.2

C₈H₂₀BCaCa[B(C₂H₅)₄]

Formation: 5.4.3.2.2

C₈H₂₀BClN₂[(C₂H₅)₂N]₂BClReactions with R₃SiK: 5.3.7.4.1Reaction with Li[R₃Sn]: 5.3.17.2.2**C₈H₂₀BCIS**(CH₃)₂CHC(CH₃)₂BHCl·S(CH₃)₂

Formation: 5.3.2.5.1

Hydroboration of alkenes directive ef-
fects: 5.3.2.5.1**C₈H₂₀BSr**Sr[B(C₂H₅)₄]

Formation: 5.4.3.2.2

C₈H₂₀BaZnBa[Zn(C₂H₅)₄]Exchange with SnPh₄: 5.4.3.4.4

Reaction with RC≡CH: 5.4.3.4.2

Reaction with olefins and enynes:
5.4.3.4.1(C₂H₅)₂Ba·Zn(C₂H₅)₂

Formation: 5.4.3.2.2

C₈H₂₀Be₂FKKF[Be(C₂H₅)₂]₂Use in isolation of BeEt₂: 5.4.3.3.1**C₈H₂₀BrMgN**C₂H₅MgBr·N(C₂H₅)₃Reaction with Ph₃SnH: 5.4.6.5**C₈H₂₀CaZn**Ca[Zn(C₂H₅)₄]

Reaction with RC≡CH: 5.4.3.4.2

Reaction with olefins and enynes:
5.4.3.4.1(C₂H₅)₂Ca·Zn(C₂H₅)₂

Formation: 5.4.3.2.2

C₈H₂₀GaKK[(C₂H₅)₄Ga]

Formation: 5.3.4.5.4

C₈H₂₀GaLiLi[(C₂H₅)₄Ga]

Formation: 5.3.4.3.1

C₈H₂₀N₂O₄SO₂S[N(C₂H₅)₂]₂

Solvent: 5.4.2.2.1

C₈H₂₀O₄TiTi(OC₂H₅)₄Catalyst for isomerization of R₃Al:
5.3.3.5.3**C₈H₂₀Pb**(C₂H₅)₄Pb

Formation: 5.4.7.2.4

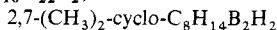
- Reaction with Ca, Li and Na metals:
5.4.7.2.3
- C₈H₂₀Si**
(C₂H₅)₄Si
Reaction with GaX₃: 5.3.4.3.1
- C₈H₂₀Sn**
(C₂H₅)₄Sn
Reaction with BX₃: 5.3.2.3.1
- C₈H₂₀SrZn**
(C₂H₅)₂Sr·Zn(C₂H₅)₂
Formation: 5.4.3.2.2
Sr[Zn(C₂H₅)₄]
Exchange with SnPh₄: 5.4.3.4.4
Reaction with RC≡CH: 5.4.3.4.2
Reaction with olefins and enynes:
5.4.3.4.1
- C₈H₂₁AlClKS**
K[(n-C₄H₉)₂(Cl)AlSiH₃]
Formation: 5.3.8.2.1
- C₈H₂₁AlSi**
(n-C₄H₉)₂AlSiH₃
Formation: 5.3.8.2.1
- C₈H₂₁Al₃**
[(CH₃)₂Al]₃CCH₃
Formation and decomposition: 5.3.3.4.1,
5.3.3.5.4
- C₈H₂₁B₈FeNa**
Na[(CH₃)₂C₂B₄H₄]₂FeH
Reaction with SnCl₂: 5.3.17.3.2
- C₈H₂₁BeBrN₂**
C₂H₅BeBr·(CH₃)₂NCH₂CH₂N(CH₃)₂
Formation: 5.4.3.3.2
- C₈H₂₁Br₂InN₂**
C₂H₅InBr₂·(CH₃)₂NC₂H₄N(CH₃)₂
Formation: 5.3.5.3.3
- C₈H₂₁GaN₂**
[(CH₃)₄N][(CH₃)₃GaCN]
Formation: 5.3.4.5.3
- C₈H₂₁GaSi**
(C₂H₅)₂GaCH₂Si(CH₃)₃
Formation: 5.3.4.3.4
- C₈H₂₁LiMg₂**
LiMg₂H₃[(CH₂)₃CH₃]₂
Formation: 5.4.2.4.3
- C₈H₂₁SnTl**
(CH₃)₂TlSn(C₂H₅)₃
Formation: 5.3.21.1
- C₈H₂₂B₂**
(C₂H₅)₂BH₂B(C₂H₅)₂
Redistribution: 5.3.2.5.3
- C₈H₂₂B₈**
5,5'-[(CH₃)₂C₂B₄H₅]₂
Reaction with benzene: 5.3.2.7.6
- C₈H₂₂BeSi₂**
[(CH₃)₃SiCH₂]₂Be
Formation: 5.4.3.4.4
- C₈H₂₂BrGaSi₂**
[(CH₃)₃SiCH₂]₂GaBr
Formation: 5.3.4.3.5
- C₈H₂₂ClGaSi₂**
[(CH₃)₃SiCH₂]₂GaCl
Formation: 5.3.4.3.5
- C₈H₂₂ClInSi₂**
[(CH₃)₃SiCH₂]₂InCl
Formation: 5.3.5.3.2
- C₈H₂₂HgSi₂**
[(CH₃)₃SiCH₂]₂Hg
Reaction with Al metal: 5.3.3.2.3
- C₈H₂₂MgSi₂**
[(CH₃)₃SiCH₂]₂Mg
Formation: 5.4.2.3.2
- C₈H₂₄Al₂Be**
Be[Al(CH₃)₄]₂
Formation: 5.4.3.4.4
- C₈H₂₄Al₂Mg**
Mg[(CH₃)₄Al]₂
Formation Structure: 5.3.3.5.4
- C₈H₂₄AsGa**
[(CH₃)₄As][Ga(CH₃)₄]
Formation: 5.3.4.5.4
- C₈H₂₄B₂N₄**
[(CH₃)₂N]₂BB[N(CH₃)₂]₂
Formation: 5.3.7.3.1
- C₈H₂₄B₄Si₂**
μ,4-[(CH₃)₃Si]₂C₂B₄H₆
Formation: 5.3.7.3.2
- C₈H₂₄Be₂N₂**
C₂H₅BeH·2 N(CH₃)₃
Reaction with olefins: 5.4.3.4.3
- C₈H₂₄Be₄O₄**
(CH₃BeOCH₃)₄
Redistribution: 5.4.3.3.2
- C₈H₂₄In₂N₂**
[(CH₃)₂InN(CH₃)₂]₂
Formation: 5.3.5.4.2
Reaction with C₅H₆: 5.3.5.4.2
- C₈H₂₄LiSn₂Tl**
Li{[(CH₃)₃Sn]₂Tl(CH₃)₂]
Formation: 5.3.21.3
- C₈H₂₄N₂P₂Si**
(CH₃)₂Si[N=P(CH₃)₃]₂
Reaction with Me₃Al·OEt₂: 5.3.3.5.4
- C₈H₂₄O₄Si₄**
[(CH₃)₂SiO]₄
Reaction with GaX₃: 5.3.4.3.2

- C₈H₂₆Be₂N₂**
 $[\text{CH}_3\text{BeH}\cdot\text{N}(\text{CH}_3)_3]_2$
 Reaction with 1-decene: 5.4.3.4.3
- C₈H₂₈B₁₀S**
 $\text{B}_{10}\text{H}_{11}(\text{C}_6\text{H}_{11})[\text{S}(\text{CH}_3)_2]$
 Formation: 5.3.2.7.1
- C₈H₂₈Ga₄O₄**
 $[(\text{CH}_3)_2\text{GaOH}]_4$
 Formation: 5.3.4.5.3
- C₈H₃₂B₁₀S₂**
 $[(\text{C}_2\text{H}_5)_2\text{S}]_2\text{B}_{10}\text{H}_{12}$
 Reaction with acetylene: 5.3.2.7.3
 Reaction with ethyl isocyanide: 5.3.2.7.4
- C₈K**
 KC_8
 Reaction with MgX_2 : 5.4.2.3.1
- C₉H₃F₁₀O₆S₂Tl**
 $4\text{-CH}_3\text{C}_6\text{F}_4\text{Tl}(\text{O}_3\text{SCF}_3)_2$
 Formation: 5.3.6.3.4
- C₉H₃F₁₀O₇S₂Tl**
 $4\text{-CH}_3\text{OC}_6\text{F}_4\text{Tl}(\text{O}_3\text{SCF}_3)_2$
 Formation: 5.3.6.3.4
- C₉H₆BBr₂MnO₃**
 $\text{h}^5\text{-CH}_3\text{C}_5\text{H}_3\text{BBr}_2\text{Mn}(\text{CO})_3$
 Formation: 5.3.2.3.3
- C₉H₆BI₂MnO₃**
 $\text{h}^5\text{-CH}_3\text{C}_5\text{H}_3\text{BI}_2\text{Mn}(\text{CO})_3$
 Formation: 5.3.2.3.3
- C₉H₆CrO₃**
 $\text{h}^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$
 Reaction with MeB: 5.3.2.3.2
- C₉H₇BI MnO₃**
 $\text{h}^5\text{-C}_5\text{H}_4\text{BCH}_3\text{IMn}(\text{CO})_3$
 Formation: 5.3.2.3.3
- C₉H₇BrMg**
 $\text{C}_9\text{H}_7\text{MgBr}$
 Pyrolysis: 5.4.2.3.2
- C₉H₇CaI**
 $(\text{Indenyl})\text{CaI}$
 Formation: 5.4.3.4.2
- C₉H₇ClMg**
 $\text{C}_9\text{H}_7\text{MgCl}$
 Formation: 5.4.2.3.2
- C₉H₇MnO₃**
 $\text{h}^5\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$
 Reaction with BX_3 : 5.3.2.3.3
- C₉H₉BCl**
 $(\text{o-C}_6\text{H}_4)\text{C}(\text{CH}_3)\text{CH}_2\text{BCl}$
 Formation: 5.3.2.3.6
- C₉H₉BrMg**
 $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{MgBr}$
 Formation: 5.4.2.3.1
- C₉H₉BrMgO₂S**
 $\text{CH}_3\text{CH}=\text{C}(\text{MgBr})\text{SO}_2\text{C}_6\text{H}_5$
 Formation: 5.4.2.3.1
- C₉H₉K**
 $\text{K}[\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2]$
 Reaction with MgX_2 : 5.4.2.3.1
- C₉H₉LiO₂S**
 $\text{CH}_3\text{CH}=\text{CLiSO}_2\text{C}_6\text{H}_5$
 Reaction with MgX_2 : 5.4.2.3.1
- C₉H₁₀MgO**
 $\text{CH}_2=\text{CHCH}_2\text{MgOC}_6\text{H}_5$
 Formation: 5.4.2.2.1
- C₉H₁₁BrMg**
 $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{CMgBr}$
 Formation: 5.4.2.3.1
 $2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2\text{MgBr}$
 Formation: 5.4.2.2.1
- C₉H₁₁ClMg**
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{MgCl}$
 Formation: 5.4.2.5.1
- C₉H₁₄Be**
 $\text{h}^5\text{-C}_5\text{H}_5\text{BeC}(\text{CH}_3)_3$
 Formation: 5.4.3.4.4
- C₉H₁₄BrMgO**
 1-bromomagnesi-7-exthoxynorbornane
 Stability: 5.4.2.2.1
- C₉H₁₄MgSi**
 $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiMgCH}_3$
 Formation: 5.4.4.7
- C₉H₁₄Si**
 $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$
 Reaction with GaX_3 : 5.3.4.3.1
 8,8-dimethyl-8-silabicyclo[3.2.1]octa-2,6-diene
 Formation: 5.4.2.2.4
- C₉H₁₅Al**
 $(\text{cyclo-C}_3\text{H}_5)_3\text{Al}$
 Formation: 5.3.3.2.3
 $(\text{C}_3\text{H}_5)_3\text{Al}$
 Transmetalation: 5.3.3.5.4
- C₉H₁₅Al₂Br₃**
 $(\text{H}_2\text{C}=\text{CHCH}_2)_3\text{Al}_2\text{Br}_3$
 Reaction with $\text{B}(\text{OR})_3$: 5.3.2.4.3
- C₉H₁₅B**
 $(\text{CH}_2\text{CH}=\text{CH}_2)_3\text{B}$
 Formation: 5.3.2.4.3
 1-B-tricyclo[3.3.1.1^{3,7}]C₉H₁₅
 Formation: 5.3.2.5.1
- C₉H₁₅BO₂**
 $\text{OCH}_2\text{CH}_2\text{OBCHCH}_2\text{CH}_2\text{CMe}=\text{CHC}^*\text{H}_2$
 Formation: 5.3.2.6.4

- 4,4,6-Me₃-cyclo-C₃H₃O₂BCH=C=CH₂
Formation: 5.3.2.4
- C₉H₁₅BeN**
h⁵-C₅H₅BeN(C₂H₅)₂
Formation: 5.4.3.3.2
- C₉H₁₅Ga**
(CH₂=CHCH₂)₃Ga
Formation: 5.3.4.2.3
(cyclo-C₃H₅)₃Ga
Formation: 5.3.4.2.3
(C₂H₅)₂GaC₅H₅-h¹
Formation: 5.3.4.3.1
- C₉H₁₅In**
(CH₂=CHCH₂)₃In
Formation: 5.3.5.3.3
- C₉H₁₆Si**
h¹-CH₃C₅H₄Si(CH₃)₃
Reaction with BX₃: 5.3.2.3.1
- C₉H₁₇B**
1-B-bicyclo[4.4.0]C₉H₁₇
Formation and thermal isomerization:
5.3.2.5.1
- C₉H₁₇BO**
9-CH₃OB-bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.5.1
Reaction with Li[R₃Si]: 5.3.7.4.3
- C₉H₁₇BrMg**
CH₂(CH₂)₇CHMgBr
Formation: 5.4.2.2.1
- C₉H₁₈AlN**
(CH₂=CH)₃Al·N(CH₃)₃
Formation: 5.3.3.2.3, 5.3.3.4.4
(i-C₄H₉)₂AlCN
Formation: 5.3.3.5.2
- C₉H₁₈BNa**
Na[(C₂H₅)₃BC≡CCH₃]
Reaction with R₂BCl: 5.3.2.3.2
- C₉H₁₈B₂O₆**
(OCH₂CH₂CH₂OBOCH₂)₂CH₂
Reaction with R₃B: 5.3.2.6.1
- C₉H₁₈LiN**
2,2,6,6-(CH₃)₄C₅H₆N·Li
Reaction with R₃B: 5.3.2.3.2
- C₉H₁₈Mg₃O₃**
(OCH₂CH₂CH₂Mg)₃
Decomposition: 5.4.2.2.1
- C₉H₁₉B**
HBCH[C(CH₃)₃]CH₂C(CH₃)₂
Formation: 5.3.2.6.3
- C₉H₁₉IO₂Sr**
CH₃ISr·2 OCH₂CH₂CH₂CH₂
Formation: 5.4.3.2.1
- C₉H₂₁Al**
(i-C₃H₇)₃Al
Formation: 5.3.3.2.3
Isomerization: 5.3.3.5.3
Reaction with olefins: 5.3.3.5.1
(n-C₃H₇)₃Al
Alumination of alkynes: 5.3.3.5.2
Formation: 5.3.3.2.1, 5.3.3.2.3, 5.3.3.3.2, 5.3.3.4.2
Formation via isomerization: 5.3.3.5.3
Growth reaction with C₂H₄: 5.3.3.5.1
Pyrolysis: 5.3.3.5.3
Reaction with propene: 5.3.3.5.1
- C₉H₂₁B**
(C₃H₇)₃B
Reaction with BeEt₂: 5.4.3.4.4
- C₉H₂₁BO**
(n-C₄H₉)₂BOCH₃
Reaction with RLi: 5.3.2.4.3
- C₉H₂₁Br₃In₂**
(n-C₃H₇)₃In₂Br₃
Formation: 5.3.5.2.1
- C₉H₂₁Ga**
(i-C₃H₇)₃Ga
Formation: 5.3.4.2.3, 5.3.4.3.1
(n-C₃H₇)₃Ga
Formation: 5.3.4.2.2, 5.3.4.2.3, 5.3.4.3.1
Reaction with RLi: 5.3.4.5.4
- C₉H₂₁I₃In₂**
(n-C₃H₇)₃In₂I₃
formation: 5.3.5.2.1
- C₉H₂₁In**
(i-C₃H₇)₃In
Formation: 5.3.5.2.3
(n-C₃H₇)₃In
Formation: 5.3.5.2.3, 5.3.5.3.1
- C₉H₂₂BKO₃**
K[(i-C₃H₇O)₃BH]
Reduction of hexylalkylchloroboranes:
5.3.2.5.1
- C₉H₂₃BeN**
CH₃Be[CH₂C(CH₃)₃]·N(CH₃)₃
Formation: 5.4.3.4.4
- C₉H₂₄AlN**
(C₂H₅)₃Al·N(CH₃)₃
Reaction with H₃Al·NR₃: 5.3.3.4.3
- C₉H₂₄B₄O₈**
C[B(OCH₃)₂]₄
Formation: 5.3.2.3.2
- C₉H₂₄BeO₂**
CH₃BeH·2 O(C₂H₅)₂
Formation: 5.4.3.3.2

- C₉H₂₇AlSi₃**
Al[Si(CH₃)₃]₃
Formation: 5.3.8.6
- C₉H₂₇Be₃N₃**
[CH₃BeN(CH₃)₂]₃
Reaction with PY: 5.4.3.3.2
- C₉H₂₇GaSi₃**
Ga[Si(CH₃)₃]₃
Formation: 5.3.9
- C₉H₂₇InSi₃**
In[Si(CH₃)₃]₃
Formation: 5.3.10
- C₉H₂₇NSi₃**
[(CH₃)₃Si]₃N
Reaction with BX₃: 5.3.2.3.1
- C₉H₂₇PSi₃**
P[Si(CH₃)₃]₃
Reaction with Al metal and Hg(SiR₃)₂:
5.3.8.3
- C₉H₂₇Si₃Tl**
Tl[Si(CH₃)₃]₃
Formation: 5.3.11.2
Reaction with CHCl₃: 5.3.11.2
- C₁₀H₆Co₂O₆**
(CH₃C≡CCH₃)Co₂(CO)₆
Hydroboration catalyst: 5.3.2.7.1
- C₁₀H₇BrMg**
1-C₁₀H₇MgBr
Formation: 5.4.2.2.1
- C₁₀H₇CaI**
C₁₀H₇CaI
Formation: 5.4.3.2.1
- C₁₀H₇ISr**
1-C₁₀H₇SrI
Formation: 5.4.3.2.1
- C₁₀H₈**
naphthalene
Reaction with Na[R₄Al] in THF:
5.3.3.5.4
- C₁₀H₈B₂Br₄Fe**
(h⁵-C₅H₄BBR₂)₂Fe
Formation: 5.3.2.3.3
- C₁₀H₈B₂FeI₄**
(h⁵-C₅H₄BI₂)₂Fe
Formation: 5.3.2.3.3
- C₁₀H₈B₂Cl₄**
C₁₀H₈(BCl₂)₄
Formation: 5.3.2.3.4
- C₁₀H₈Br₂FeMg₂**
Fe(C₅H₄MgBr-h⁵)₂
Formation: 5.4.2.3.1
- C₁₀H₈FeNa₂**
Fe(C₅H₄Na-h⁵)₂
Reaction with MgX₂: 5.4.2.3.1
- C₁₀H₈N₂**
2,2'-(C₅H₄N)₂
Reaction with R₃Al: 5.3.3.5.4
- C₁₀H₈Na**
Na[C₁₀H₈]
Reaction with RX and MgX₂: 5.4.2.3.1
Used to form activated Mg: 5.4.2.2.1
- C₁₀H₉BBR₃Fe**
h⁵-C₅H₅FeC₅H₄BBR₂-h⁵
Formation: 5.3.2.3.3
- C₁₀H₉BFeI₂**
h⁵-C₅H₅FeC₅H₄BI₂-h⁵
Formation: 5.3.2.3.3
- C₁₀H₉BIMnO₃**
h⁵-CH₃C₅H₃BCH₃IMn(CO)₃
Formation: 5.3.2.3.3
- C₁₀H₉FeI**
h⁵-C₅H₅FeC₅H₄I-h⁵
Reaction with TiCl₄: 5.3.6.3.2
- C₁₀H₁₀Be**
h⁵-C₅H₅BeC₅H₅-h¹
Formation: 5.4.3.3.1
Reaction with Be(NR₂)₂: 5.4.3.3.2
- C₁₀H₁₀Ca**
(C₅H₅)₂Ca
Formation: 5.4.3.2.3
(h¹-C₅H₅)₂Ca
Formation: 5.4.3.4.2
- C₁₀H₁₀Cl₂Ti**
(h⁵-C₅H₅)₂TiCl₂
Catalyst for addition of MgH₂ to alkynes: 5.4.2.4.1
Catalyst for addition of MgH₂ to olefins: 5.4.2.4.1
Catalyst for decomposition of R₃Al: 5.3.3.5.3
Catalyst for hydroalumination: 5.3.3.4.1
Catalyst for reaction of MgH₂ with alkynes: 5.4.2.4.2
- C₁₀H₁₀Cl₂Zr**
(h⁵-C₅H₅)₂ZrCl₂
Catalyst for carbalumination of alkynes: 5.3.3.5.1
From (h⁵-C₅H₅)₂ZrRCl: 5.3.3.3.1
- C₁₀H₁₀Co**
(h⁵-C₅H₅)₂Co
Reaction with PhBCl₂: 5.3.2.3.4
- C₁₀H₁₀Fe**
(h⁵-C₅H₅)₂Fe
Reaction with MeB: 5.3.2.3.2
Reaction with BX₃: 5.3.2.3.3
- C₁₀H₁₀Hg**
(h⁵-C₅H₅)₂Hg
Reaction with Tl metal: 5.3.6.2.6

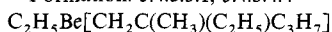
- C₁₀H₁₀IlI**
(C₅H₅)₂IlI
Formation: 5.3.5.3.2
- C₁₀H₁₀Mg**
(C₅H₅)₂Mg
Formation: 5.4.2.3.2
Redistribution with MgH₂: 5.4.2.4.3
(h⁵-C₅H₅)₂Mg
Formation: 5.4.2.2.5
- C₁₀H₁₀Sn**
(C₅H₅)₂Sn
Reaction with BX₃: 5.3.17.4
(h⁵-C₅H₅)₂Sn
Reaction with RMgX: 5.4.6.6
- C₁₀H₁₁Tl**
(CH₃)₂TlC≡CC₆H₅
Formation: 5.3.6.4.1
- C₁₀H₁₂MgN₂**
(NC₅H₆)₂Mg
Formation: 5.4.2.4.1
- C₁₀H₁₃AlO**
(HC≡C)₃Al·O(C₂H₅)₂
Formation: 5.3.3.3.1
- C₁₀H₁₃B**
CH₂(CH₂)₃B·C₆H₅
Formation: 5.3.2.5.1
- C₁₀H₁₃BeClO₂**
C₆H₅BeCl·OC₄H₉O
Formation: 5.4.3.3.2
- C₁₀H₁₃CaIO₂**
C₆H₅ICa·OCH₂CH₂OCH₂CH₂
Formation and stability: 5.4.3.2.1
- C₁₀H₁₅Al**
(C₂H₅)₂AlC₆H₅
Formation: 5.3.3.5.4
- C₁₀H₁₆**
(CH₃)₂C=CH(CH₂)₂C=CH₂(CH=C*
H₂)
Reaction with Sia₂BH: 5.3.2.5.1
- C₁₀H₁₆AlK**
K[(C₂H₅)₂C₆H₅AlH]
Formation: 5.3.3.5.4
- C₁₀H₁₆B₄**
4-C₆H₅-2,3-(CH₃)₂-nido-2,3-C₂B₄H₅
Formation: 5.3.2.7.6
- C₁₀H₁₆Mg**
(C₅H₉)₂Mg
Formation: 5.4.2.3.3
- C₁₀H₁₆N₄**
(C₄H₈CN)₂N₂
Radical starter: 5.3.2.3.3
- C₁₀H₁₇AlO**
(CH₂=CH)₃Al·OC₄H₉
Formation: 5.3.3.2.3
- C₁₀H₁₈Al₂**
[(CH₃)₂Al(C≡CCH₃)]₂
Reaction with Be(C≡CMe)₂: 5.4.3.4.4
- C₁₀H₁₈BCl**
9-Cl(CH₂)₂B-bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.5.1
- C₁₀H₁₈BI**
(cyclo-C₅H₉)₂BI
Formation: 5.3.2.5.1
- C₁₀H₁₈ClMg**
(CH₃)₂C=CH(CH₂)₂(CH₃)CH=CHC*
H₂MgCl
Formation: 5.4.2.3.2
- C₁₀H₁₈Ge**
(C₂H₅)₃GeC≡CCH=CH₂
Reaction with RCaX, RBaX: 5.4.3.4.1
- C₁₀H₁₉Al**
(CH₃)₂AlC≡CC₆H₁₃-n
Reaction with R₃Al: 5.3.3.5.1
- C₁₀H₁₉AlO**
(CH₂=CH)₃Al·O(C₂H₅)₂
Formation: 5.3.3.2.3
- C₁₀H₁₉B**
{2,6,6-(CH₃)₃-bicyclo[3.1.1]C₇H₈}BH₂
Formation: 5.3.2.5.1
Hydroborating agent: 5.3.2.5.1
9-C₂H₅B-bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.5.1
- C₁₀H₁₉BLi**
Li[CH₃CB(CH₃)C[C(CH₃)₃]CH₂CH₂]
Reaction with SnCl₂: 5.3.17.3.3
- C₁₀H₁₉BO₂**
HC≡CB[O(CH₂)₃CH₃]₂
Formation: 5.3.2.4.1
- C₁₀H₁₉Ga**
(C₂H₅)₂GaC≡CC₄H₉-n
Formation: 5.3.4.5.1
- C₁₀H₂₀Mg₂**
CH₂(CH₂)₄Mg(CH₂)₅Mg
Formation: 5.4.2.2.2
- C₁₀H₂₁BO₂**
H₂C=CHB(OC₄H₉-n)₂
Reaction with RMgX: 5.3.2.4.2
Reaction with dienes: 5.3.2.6.4
- C₁₀H₂₁Ga**
(C₂H₅)₂GaC(C₂H₅)=CHCH₂CH₃
Formation: 5.3.4.4.1
- C₁₀H₂₁IO₂Sr**
C₂H₅ISr·2 OCH₂CH₂CH₂CH₂
Formation: 5.4.3.2.1
- C₁₀H₂₂B₂**
[CH₂(CH₂)₄BH]₂
Formation: 5.3.2.5.1, 5.3.2.6.1, 5.3.2.6.2

C₁₀H₂₂B₂, *contd*

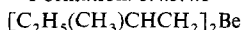
Formation: 5.3.2.5.1

C₁₀H₂₂Be

Formation: 5.4.3.3.1, 5.4.3.4.4

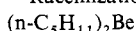


Formation: 5.4.3.4.1



Formation: 5.4.3.3.1

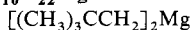
Racemization: 5.4.3.4.3



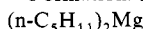
Formation: 5.4.3.3.1

C₁₀H₂₂Hg

Reaction with Al metal: 5.3.3.2.3

C₁₀H₂₂Mg

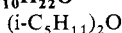
Formation: 5.4.2.3.2



Formation: 5.4.2.3.1

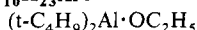
Properties in hydrocarbon solution:

5.4.2.3.2

C₁₀H₂₂O

Catalyst for reaction of Ga metal with

RX: 5.3.4.2.2

C₁₀H₂₃AlO

Formation: 5.3.3.5.3

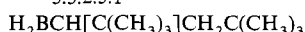
C₁₀H₂₃B

Formation: 5.3.2.5.1, 5.3.2.6.1

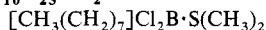
Hydroboration of alkenes and alkynes,
directive effects: 5.3.2.5.1

Reactivity toward functional groups:

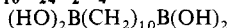
5.3.2.5.1



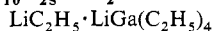
Formation: 5.3.2.6.3

C₁₀H₂₃BCl₂S

Formation: 5.3.2.5.1

C₁₀H₂₄B₂O₄

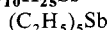
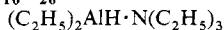
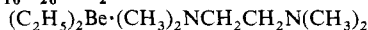
Formation: 5.3.2.4.1

C₁₀H₂₅GaLi₂

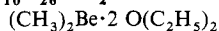
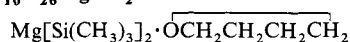
Li(7) and H NMR: 5.3.4.5.2

C₁₀H₂₅GaO

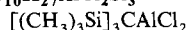
Formation: 5.3.4.2.2

C₁₀H₂₅SbExchange with R₃Al: 5.3.3.5.4**C₁₀H₂₆AlN**Bis-metallation of C₂H₂: 5.3.3.5.2**C₁₀H₂₆BeN₂**

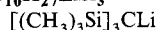
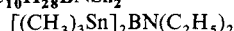
Reaction with PhC≡CH: 5.4.3.4.2

C₁₀H₂₆BeO₂Metallation of B₉C₂H₁₃: 5.4.3.4.2**C₁₀H₂₆MgOSi₂**

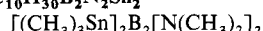
Formation: 5.4.4.4

C₁₀H₂₇AlCl₂Si₃

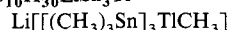
Formation: 5.3.3.3.1

C₁₀H₂₇LiSi₃Reaction with AlCl₃: 5.3.3.3.1**C₁₀H₂₆BNSn₂**

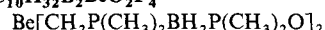
Formation: 5.3.17.2.2

C₁₀H₃₀B₂N₂Sn₂

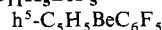
Formation: 5.3.17.2.2

C₁₀H₃₀LiSn₃Tl

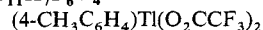
Formation: 5.3.21.3

C₁₀H₃₂B₂BeO₂P₄

Formation: 5.4.3.3.1

C₁₁H₅BeF₅

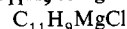
Formation: 5.4.3.4.4

C₁₁H₇F₆O₄Tl

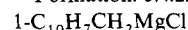
Rearrangement: 5.3.6.3.4

C₁₁H₉BrMg

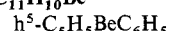
Formation: 5.4.2.3.1

C₁₁H₉ClMg

Formation: 5.4.2.3.1



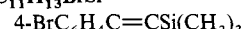
Formation: 5.4.2.2.1

C₁₁H₁₀Be

Formation: 5.4.3.3.1

C₁₁H₁₂BFel

Formation: 5.3.2.3.3

C₁₁H₁₃BrSi

Formation: 5.4.2.2.1

- C₁₁H₁₃ClZr**
 (h₅-C₅H₅)₂ZrCH₃Cl
 Reaction with alkynes: 5.3.3.5.1
- C₁₁H₁₄AlN**
 (CH₂=CH)₃Al·NC₅H₅
 Formation: 5.3.3.2.3
- C₁₁H₁₅B**
 o-C₆H₄B(C₂H₅)CH₂CHCH₃
 Exchange with R₃Al: 5.3.3.5.4
 Formation: 5.3.3.5.4
 3-CH₃-cyclo-C₄H₇B-C₆H₅
 Formation: 5.3.2.5.1
- C₁₁H₁₅CaIO₂**
 (2-CH₃C₆H₄)ICa·OCH₂CH₂OCH₂CH₂
 Formation and stability: 5.4.3.2.1
 (3-CH₃C₆H₄)ICa·OCH₂CH₂OCH₂CH₂
 Formation: 5.4.3.2.1
- C₁₁H₁₅ClMg**
 C₆H₅(CH₂)₅MgCl
 Formation: 5.4.2.5.1
- C₁₁H₁₅F₆O₅Tl**
 n-C₄H₉CH(OCH₃)CH₂Tl(O₂CCF₃)₂
 Formation: 5.3.6.3.5
- C₁₁H₁₅N**
 C₆H₅CH=NC₄H₉
 o-Metallation by BeR₂: 5.4.3.4.2
- C₁₁H₁₅O₂Tl**
 CH₃(C₆H₅)Tl[OC(O)CH(CH₃)₂]
 Formation: 5.3.6.3.8
- C₁₁H₁₆BN**
 C₆H₅CH₂(CH₂)₄BH
 Formation: 5.3.2.5.1
- C₁₁H₁₉AlO**
 O(CH₂)₃AlAl(CH₂)₂CHCH₂CH₂CH=C*
 HCH₂
 Formation: 5.3.3.4.2
- C₁₁H₁₉B**
 2-C₂H₅B-tricyclo-[3.3.1.1^{3,7}]C₉H₁₄
 Formation: 5.3.2.5.1
 9-CH₂=CHCH₂B-bicyclo [3.3.1]C₈H₁₄
 Formation: 5.3.2.4.3
- C₁₁H₂₀AlLiSi**
 Li[C₆H₅(CH₃)₂SiAl(CH₃)₃]
 Formation: 5.3.8.2.1
- C₁₁H₂₁BO₂**
 CH₃C≡CB[O(CH₂)₃CH₃]₂
 Formation: 5.3.2.4.1
- C₁₁H₂₁O₅Tl**
 n-C₄H₉CH(OCH₃)CH₂Tl(O₂CCH₃)₂
 Formation: 5.3.6.3.5
- C₁₁H₂₂BeClN**
 [(CH₃)₃C]BeCl·NC₇H₁₃
 Formation: 5.4.3.3.2
- C₁₁H₂₂Si**
 (CH₃)₃SiC≡CC₆H₁₃-n
 Reaction with R₂AlCl: 5.3.3.5.1
- C₁₁H₂₂Si₂**
 1,1-C₅H₄[Si(CH₃)₃]₂
 Reaction with BX₃: 5.3.2.3.1
- C₁₁H₂₃IO₂Sr**
 n-C₃H₇ISr·2 OCH₂CH₂CH₂CH₂
 Formation: 5.4.3.2.1
- C₁₁H₂₅BO**
 n-C₃H₇(n-C₄H₉)BOC₄H₉-n
 Formation: 5.3.2.4.2
- C₁₁H₂₇BeBrN₂**
 [(CH₃)₃CCH₂]BeBr·(CH₃)₂NCH₂CH₂N*
 (CH₃)₂
 Formation: 5.4.3.3.2
- C₁₁H₂₇GaN₂**
 [(CH₃)₄N][(C₂H₅)₃GaCN]
 Formation: 5.3.4.5.3
- C₁₁H₂₉BN₂Sn**
 (CH₃)₃SnB[N(C₂H₅)₂]₂
 Formation: 5.3.17.2.2
- C₁₁H₃₀Ga₂N₂**
 [(CH₃)₄N][[(CH₃)₃Ga]₂CN]
 Formation: 5.3.4.5.3
- C₁₂BrF₁₀In**
 (C₆F₅)₂InBr
 Formation: 5.3.5.3.1
- C₁₂BrF₁₀Tl**
 (C₆F₅)₂TlBr
 Reaction with In metal: 5.3.5.2.6
 Reaction with LiC₆F₅: 5.3.6.3.1
 Reaction with organosulfonates: 5.3.6.3.9
- C₁₂ClF₁₀In**
 (C₆F₅)₂InCl
 Formation: 5.3.5.3.1
- C₁₂F₁₀IIn**
 (C₆F₅)₂InI
 Formation: 5.3.5.2.1
- C₁₂H₂F₁₀Ge**
 (C₆F₅)₂GeH₂
 Reaction with TlR₃: 5.3.16
- C₁₂H₈BCl₂F₄Tl**
 [(4-ClC₆H₄)₂Tl][BF₄]
 Formation: 5.3.6.2.5
- C₁₂H₈B₂I₂**
 (o-C₆H₄)BI(o-C₆H₄)BI
 Formation: 5.3.2.3.3
- C₁₂H₈BeCl₂**
 (4-ClC₆H₄)₂Be
 Formation: 5.4.3.4.4
- C₁₂H₈BrF₂In**
 (4-FC₆H₄)₂InBr
 Formation: 5.3.5.3.4

- C₁₂H₁₀BBr**
(C₆H₅)₂BBr
Formation: 5.3.2.3.1
- C₁₂H₁₀BBrF₄**
[(C₆H₅)₂Br][BF₄]
Reaction with Tl metal: 5.3.6.2.4
- C₁₂H₁₀BCl**
(C₆H₅)₂BCl
Formation: 5.3.2.3.1
- C₁₂H₁₀BClF₄**
[(C₆H₅)₂Cl][BF₄]
Reaction with Tl metal: 5.3.6.2.4
- C₁₂H₁₀BF₄I**
[(C₆H₅)₂I][BF₄]
Reaction with Tl metal: 5.3.6.2.4
- C₁₂H₁₀BF₄Tl**
[(C₆H₅)₂Tl][BF₄]
Formation: 5.3.6.2.4, 5.3.6.2.5
- C₁₂H₁₀BI**
(C₆H₅)₂BI
Formation: 5.3.2.3.1
- C₁₂H₁₀Ba**
(C₆H₅)₂Ba
Formation: 5.4.3.2.2
- C₁₂H₁₀Be**
(C₆H₅)₂Be
Formation: 5.4.3.2.2, 5.4.3.3.1, 5.4.3.4.4
Reaction with LiR: 5.4.3.4.4
Redistribution with BeX₂: 5.4.3.3.2
- C₁₂H₁₀BrGa**
(C₆H₅)₂GaBr
Formation: 5.3.4.3.5
- C₁₂H₁₀BrIn**
(C₆H₅)₂InBr
Formation: 5.3.5.2.5, 5.3.5.3.1, 5.3.5.3.2, 5.3.5.3.4
- C₁₂H₁₀Ca**
Ca[C₆H₅]₂
Metallation of RH: 5.4.3.4.2
Polymerization of methylmethacrylate: 5.4.3.4.1
- C₁₂H₁₀Cd**
(C₆H₅)₂Cd
Reaction with Ba metal: 5.4.3.2.2
- C₁₂H₁₀ClGa**
(C₆H₅)₂GaCl
Formation: 5.3.4.3.5
- C₁₂H₁₀ClIn**
(C₆H₅)₂InCl
Formation: 5.3.5.2.5, 5.3.5.3.4
- C₁₂H₁₀ClTl**
(C₆H₅)₂TlCl
Formation: 5.3.6.2.5
- C₁₂H₁₀GaI**
(C₆H₅)₂GaI
Formation: 5.3.4.3.5
- C₁₂H₁₀Hg**
(C₆H₅)₂Hg
Reaction with Al metal: 5.3.3.2.3
Reaction with BX₃: 5.3.2.3.1
Reaction with In metal: 5.3.5.2.5
Reaction with BeR₂: 5.4.3.4.4
Reaction with Be and Ca metals: 5.4.3.2.2
- C₁₂H₁₀IIn**
(C₆H₅)₂InI
Formation: 5.3.5.2.2, 5.3.5.3.4
- C₁₂H₁₀Mg**
(C₆H₅)₂Mg
Formation: 5.4.2.3.1, 5.4.2.3.2
Reaction with Li[AlH₄]: 5.3.3.4.4
Redistribution with MgX₂: 5.4.2.3.2
Redistribution with MgH₂: 5.4.2.4.3
- C₁₂H₁₀Sn**
(C₆H₅)₂Sn
Reaction with PhMgBr: 5.4.6.6
- C₁₂H₁₀Zn**
(C₆H₅)₂Zn
Reaction with Li[AlH₄]: 5.3.3.4.4
Reaction with BX₃: 5.3.2.3.1
- C₁₂H₁₁Al**
(C₆H₅)₂AlH
Formation: 5.3.3.4.3
Metallation of alkynes: 5.3.3.5.2
- C₁₂H₁₁B**
(C₆H₅)₂BH
Redistribution: 5.3.2.5.3
- C₁₂H₁₁BO**
(C₆H₅)₂BOH
Formation: 5.3.2.4.2
- C₁₂H₁₁BeClN₂**
C₂H₅BeCl·(NC₅H₃C₅H₃N)
Formation: 5.4.3.3.2
- C₁₂H₁₂AlLi**
Li[(C₆H₅)₂AlH₂]
Formation: 5.3.3.4.3
- C₁₂H₁₂BrMgNO**
BrMgC₆H₄C≡CNC(CH₃)₂CH₂O
Formation: 5.4.2.2.1
- C₁₂H₁₄AlNa**
Na[(CH₃)₂AlC₁₀H₈]
Formation and structure: 5.3.3.5.4
- C₁₂H₁₄B₂**
C₆H₅HBH₂BHC₆H₅
Formation: 5.3.2.5.3
- C₁₂H₁₄Mg**
(h⁵-CH₃C₅H₄)₂Mg
Formation: 5.4.2.2.5

- C₁₂H₁₄Sn**
(*h*⁵-CH₃C₅H₄)₂Sn
Reaction with RMgX: 5.4.6.6
- C₁₂H₁₅BO₂**
C₂H₅CHC(C₂H₅)BOC₆H₄O-2
Formation: 5.3.2.5.1
(E)-C₆H₄O₂BCH=CHC(CH₃)₃
Formation: 5.3.2.5.1
- C₁₂H₁₅BSi**
(CH₃)₂SiCH=CHB(C₆H₅)CH=CH
Formation: 5.3.2.3.1
- C₁₂H₁₆B**
(*o*-C₆H₄)C(CH₃)CH₂BC₃H₇
Redistribution with BCl₃: 5.3.2.3.6
- C₁₂H₁₆BeN₂O**
CH₃BeOCH₃·2 NC₅H₅
Formation: 5.4.3.3.2
- C₁₂H₁₇BO**
CH₂=CH(C₆H₅)BOC₄H₉-n
Formation: 5.3.2.4.2
- C₁₂H₁₇CaIN₂**
C₆H₅CaI·NC₆H₁₁N
Metallation of RH: 5.4.3.4.2
- C₁₂H₁₈AlN**
(CH₃C≡C)₃Al·N(CH₃)₃
Formation: 5.3.3.2.3
- C₁₂H₁₈AlNa**
Na[*o*-C₆H₄Al(C₂H₅)₂CH₂CH₂]
Formation: 5.3.3.5.4
- C₁₂H₁₈MgO₂**
[2,6-(CH₃O)₂C₆H₃]MgCH(CH₃)C₂H₅
Formation: 5.4.2.3.1
- C₁₂H₂₀Sn**
(cyclo-C₃H₅)₄Sn
Reaction with BX₃: 5.3.2.3.1
- C₁₂H₂₁Al**
(CH₂=CHCH₂CH₂)₃Al
Formation: 5.3.3.2.3
- C₁₂H₂₁AlSi**
C₆H₅(CH₃)₂SiAl(C₂H₅)₂
Formation: 5.3.8.2.1
- C₁₂H₂₁B**
(CH₃CH=CHCH₂)₃B
Isomerization: 5.3.2.6.2
1-(CH₃)₂B-adamantane
Formation: 5.3.2.4.3
9-(CH₃CH=CHCH₂)B-bicyclo[3.3.1]*
- C₈H₁₄**
Allylic rearrangement: 5.3.2.5.1
- C₁₂H₂₁BO₂**
CH₂=CHC≡CB[O(CH₂)₃CH₃]₂
Formation: 5.3.2.4.1
- C₁₂H₂₁B₃**
[(CH₂)₃BCH]₃
Formation: 5.3.2.3.2
- C₁₂H₂₁O₆Tl**
Tl[O₂CCH(CH₃)₂]₃
Thallating agent: 5.3.6.3.4
- C₁₂H₂₂B₄**
(CH₃)₆C₆B₄H₄
Formation: 5.3.2.7.3
- C₁₂H₂₂Sn₂**
1,2-C₆H₄[Sn(CH₃)₃]₂
Formation: 5.4.2.2.1
- C₁₂H₂₃B**
(cyclo-C₆H₁₁)₂BH
Formation: 5.3.2.5.1
Hydroborating agent: 5.3.2.5.1
9-CH₃(CH₂)₃B-bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.4.3
- C₁₂H₂₃B₁₀Sn**
(C₆H₅)₂SnB₁₀H₁₃
Conversion to 6-C₆H₅B₁₀H₁₃: 5.3.2.7.6
- C₁₂H₂₄B₂**
(CH₂CH₂CH₂CH₂BCH₂CH₂)₂
Formation: 5.3.2.6.1, 5.3.2.6.2
CH₂(CH₂)₃BCHMe(CH₂)₂B(CH₂)₃CH₂
Formation: 5.3.2.6.1, 5.3.2.6.2
CH₃CH₂CH₂CH(BCH₂CH₂CH₂CH₂)₂
Formation: 5.3.2.6.2
- C₁₂H₂₄Ga₄N₄**
[(CH₃)₂GaCN]₄
Formation: 5.3.4.5.3
- C₁₂H₂₅BO₂**
CH₃CH=CHCH₂B[O(CH₂)₃CH₃]₂
Formation: 5.3.2.4.1
- C₁₂H₂₅IO₂Sr**
n-C₄H₉ISr·2 OCH₂CH₂CH₂CH₂
Formation: 5.4.3.2.1
- C₁₂H₂₆BCl**
[CH₃(CH₂)₅]₂BCl
Formation: 5.3.2.5.1
- C₁₂H₂₆BI**
[CH₃(CH₂)₅]₂BI
Formation: 5.3.2.5.1
- C₁₂H₂₆B₂**
(CH₂CH₂CH₂CH₂CH₂CH₂BH)₂
Formation: 5.3.2.6.1
- C₁₂H₂₆Mg**
(*n*-C₆H₁₃)₂Mg
Formation: 5.4.2.3.2
- C₁₂H₂₇Al**
(*i*-C₄H₉)₃Al
Alumination of alkynes: 5.3.3.5.2

C₁₂H₂₇Al, *contd*(i-C₄H₉)₃Al, *contd*

Decomposition in closed system:

5.3.3.5.3

Elimination of isobutene: 5.3.3.4.2

Formation: 5.3.3.2.1

Formation via isomerisation: 5.3.3.5.3

Olefin displacement: 5.3.3.4.2

Olefin elimination: 5.3.3.2.1

Reaction with NaAlH₄: 5.3.3.4.3Reaction with B(OR)₃: 5.3.2.4.3Reaction with GeX₄: 5.3.13.5

Reaction with alkenes: 5.3.3.5.1

Reaction with cycloolefins: 5.3.3.4.2

Reaction with non-terminal olefins:

5.3.3.4.2

Reaction with styrene: 5.3.3.4.2

Reaction with terminal olefins: 5.3.3.4.2

Reaction with vinylsilanes: 5.3.3.4.2

(n-C₄H₉)₃Al

Formation: 5.3.3.2.1

Formation via isomerization: 5.3.3.5.3

(s-C₄H₉)₃Al

Isomerization: 5.3.3.5.3

(t-C₄H₉)₃Al

Formation: 5.3.3.3.1

Isomerization: 5.3.3.5.3

Reaction with olefins: 5.3.3.5.1

Reactivity towards C₂H₄: 5.3.3.5.1**C₁₂H₂₇AlO**(i-C₄H₉)₂AlOC₄H₉-n

Formation: 5.3.3.4.3

C₁₂H₂₇Al₂I₃(n-C₄H₉)₃Al₂I₃

Formation: 5.3.3.2.2

C₁₂H₂₇B[(CH₃)₂CHC(CH₃)₂]₂BH

Formation: 5.3.2.5.3

(CH₃)₂CHCH₂B[C(CH₃)₃]₂

Formation: 5.3.2.4

(i-C₄H₉)₃B

Formation: 5.3.2.4.3

Reaction with BeR₂: 5.4.3.4.4(s-C₄H₉)₃B

Formation: 5.3.2.5.1

(n-C₄H₉)₂BC₄H₉-t

Formation: 5.3.2.4.3

(n-C₄H₉)₃B

Formation: 5.3.2.5.1

Thermal decomposition: 5.3.2.6.3

(t-C₄H₉)₃BI

Formation: 5.3.2.4

C₁₂H₂₇BO₃(i-C₄H₉O)₃B

Formation: 5.3.2.4

Reaction with LiC₆H₅: 5.3.2.4(n-C₄H₉O)₃B

Reaction with RMgXRLi: 5.3.2.4.2

C₁₂H₂₇B₃O₆(i-C₄H₉OBO)₃

Reaction with RMgX: 5.3.2.4.2

C₁₂H₂₇Br₃In₂(n-C₄H₉)₃In₂Br₃

Formation: 5.3.5.2.1

C₁₂H₂₇ClMgSn(n-C₄H₉)₃SnMgCl

Formation: 5.4.6.5

C₁₂H₂₇Ga(i-C₄H₉)₃Ga

Formation: 5.3.4.3.1

Reaction with alkynes: 5.3.4.4.1

Reaction with olefins: 5.3.4.4.1, 5.3.4.4.2

(n-C₄H₉)₃Ga

Formation: 5.3.4.2.2, 5.3.4.3.1

(s-C₄H₉)₃Ga

Formation: 5.3.4.3.1

(t-C₄H₉)₃Ga

Formation: 5.3.4.3.1

Reaction with GaX₃: 5.3.4.3.5**C₁₂H₂₇I₃In₂**(n-C₄H₉)₃In₂I₃

Formation: 5.3.5.2.1

C₁₂H₂₇In(i-C₄H₉)₃In

Reaction with olefins: 5.3.5.4.1

(n-C₄H₉)₃In

Formation: 5.3.5.2.3

(s-C₄H₉)₃In

Formation: 5.3.5.2.3

C₁₂H₂₇LiSnLiSn(C₄H₉-n)₃Reaction with AlR₃ or R₂AlX: 5.3.18.3**C₁₂H₂₇Tl**(n-C₄H₉)₃Tl

Formation: 5.3.6.4.2

C₁₂H₂₈AlLiLi[(i-C₄H₉)₃AlH]

Formation: 5.3.3.4.1

Li[(n-C₃H₇)₄Al]• Reaction with AlCl₃: 5.3.3.3.2**C₁₂H₂₈AlNa**Na[(i-C₄H₉)₃AlH]

Reaction with alkynes: 5.3.3.5.2

C₁₂H₂₈B₂[(C₂H₅)₂BCH₂CH₂]₂

Thermal decomposition: 5.3.2.6.1

C₁₂H₂₈BeO(t-C₄H₉)₂Be·O(C₂H₅)₂Removal of Et₂O: 5.4.3.3.1

- C₁₂H₂₈Be₂**
[C₂H₅BeC(CH₃)₃]₂
Formation: 5.4.3.4.4
- C₁₂H₂₈GaLi**
Li[(n-C₃H₇)₄Ga]
Formation: 5.3.4.5.4
- C₁₂H₂₈Sn**
(n-C₄H₉)₃SnH
Reaction with RMgX reagents: 5.4.6.5
- C₁₂H₂₉AlN₂**
[(i-C₃H₇)₃N]₂AlH
Hydroalumination reagent: 5.3.3.4.1
- C₁₂H₂₉BeBrO₂**
t-C₄H₉BeBr · 2 O(C₂H₅)₂
Formation: 5.4.3.3.2
- C₁₂H₂₉BeClO₂**
t-C₄H₉BeCl · 2 O(C₂H₅)₂
Formation by redistribution: 5.4.3.3.2
- C₁₂H₃₀AlN**
(C₂H₅)₃Al · N(C₂H₅)₃
Reaction with alkynes: 5.3.3.5.2
- C₁₂H₃₀Al₂**
(C₂H₅)₆Al₂
Reaction with InX₃: 5.3.5.3.1
- C₁₂H₃₀Al₃Cl₆Ga**
Ga[(C₂H₅)₂AlCl]₃
Formation: 5.3.4.3.1
- C₁₂H₃₀B₂**
(n-C₃H₇)₂BH₂B(C₃H₇-n)₂
Redistribution: 5.3.2.5.3
- C₁₂H₃₀BeN₂**
CH₃Be[CH₂C(CH₃)₃] · (CH₃)₂NC*
H₂CH₂N(CH₃)₂
Formation: 5.4.3.4.4
- C₁₂H₃₀BeO₂**
(C₂H₅)₂Be · 2 O(C₂H₅)₂
Metallation of B₉C₂H₁₃: 5.4.3.4.2
- C₁₂H₃₀BrGaGe₂**
BrGa[(C₂H₅)₃Ge]₂
Possible formation: 5.3.14
- C₁₂H₃₀Sn₂**
(CH₃CH₂)₃SnSn(CH₂CH₃)₃
Reaction with RMgX: 5.4.6.4
- C₁₂H₃₁BSi₂**
[(CH₃)₃SiCH(C₂H₅)₂]BH
Formation: 5.3.2.5.3
- C₁₂H₃₂Al₂Ba**
Ba[AlH(C₂H₅)₃]₂
Formation: 5.4.3.3.1
- C₁₂H₃₂B₁₀Br₁₀N₂**
[(C₂H₅)₃NH]₂B₁₀Br₁₀
Thermal decomposition: 5.3.2.7.6
- C₁₂H₃₂In₂P₂**
[In(CH₃)₂CH₂P(CH₃)₂CH₂]₂
Formation: 5.3.5.4.2
- C₁₂H₃₃AlSi₃**
[(CH₃)₃SiCH₂]₃Al
Formation: 5.3.3.2.3
- C₁₂H₃₃BSi₃**
[(CH₃)₃SiCH₂]₃B
Reaction with BeR₂: 5.4.3.4.4
- C₁₂H₃₃ClMgPbSi₃**
[(CH₃)₃SiCH₂]₃PbMgCl
Formation: 5.4.7.2.5
- C₁₂H₃₃GaSi₃**
[(CH₃)₃SiCH₂]₃Ga
Formation: 5.3.4.3.1
- C₁₂H₃₃InSi₃**
[(CH₃)₃SiCH₂]₃In
Formation: 5.3.5.3.1
- C₁₂H₃₃InSi₃**
[(CH₃)₃SiCH₂]₃In
Reaction with InX₃: 5.3.5.3.2
- C₁₂H₃₄GeSi₃**
[(CH₃)₃SiCH₂]₃GeH
Reaction with TIR₃: 5.3.16
- C₁₂H₃₄MgN₂Si₂**
Mg[Si(CH₃)₃]₂ · (CH₃)₂NCH₂CH₂N(C*H₃)₂
Formation: 5.4.4.4
- C₁₂H₃₄Si₃Sn**
[(CH₃)₃SiCH₂]₃SnH
Reaction with TIR₃: 5.3.21.1
- C₁₂H₃₆AlKSi₄**
K[Al[Si(CH₃)₃]₄]
Formation: 5.3.8.5
- C₁₂H₃₆AlLiSi₄**
Li[Al[Si(CH₃)₃]₄]
Formation: 5.3.8.4
- C₁₂H₃₆AlNaSi₄**
Na[Al[Si(CH₃)₃]₄]
Formation: 5.3.8.5
Reaction with AlCl₃: 5.3.8.6
- C₁₂H₃₆BLiSi₄**
Li[B[Si(CH₃)₃]₄]
Formation: 5.3.7.4.3
- C₁₂H₃₆B₂BeP₄**
Be[CH₂P(CH₃)₂BH₂P(CH₃)₂CH₂]₂
Formation: 5.4.3.3.1
- C₁₂H₃₆LiSn₄Tl**
Li[[CH(CH₃)₃Sn]₄Tl]
Formation: 5.3.21.3
- C₁₃H₉CaI**
(Fluorenyl)CaI
Formation: 5.4.3.4.2

- C₁₃H₁₀N₂**
(C₆H₅)₂CN₂
Reaction with Ph₃Al: 5.3.3.5.5
- C₁₃H₁₁BBr₂**
(C₆H₅)₂HCBBr₂
Formation: 5.3.2.3.3
- C₁₃H₁₁BrMg**
(C₆H₅)₂CHMgBr
Formation from K[Ph₂CH]: 5.4.2.3.1
- C₁₃H₁₁K**
K[CH(C₆H₅)₂]
Reaction with MgX₂: 5.4.2.3.1
- C₁₃H₁₂CITl**
C₆H₅(4-CH₃C₆H₄)TlCl
Formation: 5.3.6.3.3
- C₁₃H₁₅BrMg**
C₆H₅C(MgBr)(CHCH₂CH₂)₂
Formation and rearrangement: 5.4.2.3.1
- C₁₃H₁₆AlGeLi**
Li[(C₆H₅)₂CH₃GeAlH₃]
Formation: 5.3.13.4
- C₁₃H₁₇BO₂**
(CH₃)₃CCHC(CH₃)BOC₆H₄O-2
Formation: 5.3.2.5.1
- C₁₃H₁₉AlO**
(CH₃C≡C)₃Al·O(C₂H₅)₂
Formation: 5.3.3.2.3
- C₁₃H₂₁BO**
n-C₃H₇(C₆H₅)BOC₄H₉-n
Formation: 5.3.2.4.2
- C₁₃H₂₁CaIO₂**
h⁵-C₅H₅CaI·2 OC₄H₈
Formation: 5.4.3.4.2
- C₁₃H₂₃Al**
(i-C₄H₉)₂AlC₅H₅-h¹
Formation: 5.3.3.5.2
- C₁₃H₂₃B**
9-CH₃CH=CH(CH₂)₂B-bicyclo[3.3.1]*
C₈H₁₄
Formation: 5.3.2.5.1
- C₁₃H₂₅B**
7-CH₃-3-(CH₃)₃CB-bicyclo [3.3.1]C₈H₁₃
Formation: 5.3.2.4.3
- C₁₃H₂₇BSi**
(CH₃)₃Si(CH₂)₂B-bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.5.1
- C₁₃H₂₈B₂**
cis-(C₂H₅)₂B(C₂H₅)C=C(CH₃)B(C₂H₅)₂
Formation: 5.3.2.3.2
- C₁₃H₃₀B₂O**
[(CH₃)₃C]₂BB(OCH₃)[C(CH₃)₃]
Reaction with K[R₃Si]: 5.3.7.4.3
- C₁₃H₃₁AlO**
(i-C₃H₇)₃Al·O(C₂H₅)₂
Reaction with C₂H₄: 5.3.3.5.1
- C₁₃H₃₁BeN**
[(CH₃)₃CCH₂]₂Be·N(CH₃)₃
Formation: 5.4.3.3.2
Redistribution with BeR₂: 5.4.3.4.4
- C₁₃H₃₃BN₂O₃Si**
(i-C₃H₇O)₃SiB[N(CH₃)₂]₂
Formation: 5.3.7.3.1
- C₁₃H₃₅AlGe₃O**
[(CH₃)₃Ge]₃Al·OCH₂CH₂CH₂CH₂
Formation: 5.3.13.2
- C₁₃H₃₅AlOSi₃**
[(CH₃)₃Si]₃Al·OCH₂CH₂CH₂CH₂
Formation: 5.3.8.3
Reaction with R₂NCH₂CH₂NR₂: 5.3.8.3
- C₁₃H₃₅AlOSn₃**
[(CH₃)₃Sn]₃Al·OCH₂CH₂CH₂CH₂
Formation: 5.3.18.2
- C₁₃H₃₅GaOSi₃**
Ga[Si(CH₃)₃]₃·OCH₂CH₂CH₂CH₂
Formation: 5.3.9
- C₁₃H₃₆MgN₂Si₂**
Mg[Si(CH₃)₃]₂·(CH₃)₂N(CH₂)₃N(CH₃)₂
Formation: 5.4.4.4
- C₁₃H₃₇AlOSi₃**
[(CH₃)₃Si]₃Al·O(C₂H₅)₂
Formation: 5.3.8.4
Reaction with Na or K and Hg(SiR₃)₂: 5.3.8.5
- C₁₄H₉BiMnO₃**
h⁵-C₅H₄BC₆H₅IMn(CO)₃
Formation: 5.3.2.3.3
- C₁₄H₉BrMg**
(9-phenanthryl)MgBr
Formation: 5.4.2.2.1
- C₁₄H₁₀**
C₆H₅C≡CC₆H₅
Photochemical reaction with R₃Al: 5.3.3.5.4
- C₁₄H₁₀Mg**
Anthracene—Mg
Formation: 5.4.2.2.4
Reaction with R₂SnCl₂: 5.4.2.2.4
- C₁₄H₁₁BrMgO₂S**
C₆H₅CH=C(MgBr)SO₂C₆H₅
Formation: 5.4.2.3.1
- C₁₄H₁₁LiO₂S**
C₆H₅CH=CLiSO₂C₆H₅
Reaction with MgX₂: 5.4.2.3.1

- C₁₄H₁₄AlN**
 (CH₃C≡C)₃Al·NC₅H₅
 Formation: 5.3.3.2.3
- C₁₄H₁₄BF₄O₂Tl**
 [(2-CH₃OC₆H₄)₂Tl][BF₄]
 Formation: 5.3.6.2.5
 [(4-CH₃OC₆H₄)₂Tl][BF₄]
 Formation: 5.3.6.2.5
- C₁₄H₁₄BF₄Tl**
 [(2-CH₃C₆H₄)₂Tl][BF₄]
 Formation: 5.3.6.2.5
 [(4-CH₃C₆H₄)₂Tl][BF₄]
 Formation: 5.3.6.2.5
- C₁₄H₁₄Ba**
 Ba[CH₂C₆H₅]₂
 Addition to olefins: 5.4.3.4.1
 Formation: 5.4.3.2.2
 Polymerization of dienes: 5.4.3.4.1
 Polymerization of styrene: 5.4.3.4.1
- C₁₄H₁₄Be**
 (C₆H₅CH₂)₂Be
 Formation: 5.4.3.3.1
 (2-CH₃C₆H₄)₂Be
 Formation: 5.4.3.4.4
 (3-CH₃C₆H₄)₂Be
 Formation: 5.4.3.4.4
 (4-CH₃C₆H₄)₂Be
 Formation: 5.4.3.2.2, 5.4.3.3.1
- C₁₄H₁₄BrIn**
 (4-CH₃C₆H₄)₂InBr
 Formation: 5.3.5.3.4
- C₁₄H₁₄Ca**
 Ca[CH₂C₆H₅]₂
 Formation: 5.4.3.2.2
- C₁₄H₁₄Hg**
 (C₆H₅CH₂)₂Hg
 Reaction with Al metal: 5.3.3.2.3
 Reaction with Ca, Sr and Ba metals:
 5.4.3.2.2
 (2-CH₃C₆H₄)₂Hg
 Reaction with Ca metal: 5.4.3.2.2
 (3-CH₃C₆H₄)₂Hg
 Reaction with Ca metal: 5.4.3.2.2
 (4-CH₃C₆H₄)₂Hg
 Reaction with Be and Ca metals:
 5.4.3.2.2
- C₁₄H₁₄IlIn**
 (4-CH₃C₆H₄)₂InI
 Formation: 5.3.5.2.2
- C₁₄H₁₄Si**
 CH₂=CHSiH(C₆H₅)₂
 Reaction with RMgX: 5.4.2.5.1
- C₁₄H₁₄Sr**
 Sr[CH₂C₆H₅]₂
 Formation: 5.4.3.2.2
 Polymerization of dienes: 5.4.3.4.1
- C₁₄H₁₅BO**
 (2-CH₃C₆H₄)₂BOH
 Formation: 5.3.2.4.2
 (4-CH₃C₆H₄)₂BOH
 Formation: 5.3.2.4.2
- C₁₄H₁₆AlN**
 (C₆H₅)₂AlN(CH₃)₂
 Formation: 5.3.3.4.4
- C₁₄H₁₆BN**
 (C₆H₅)₂BN(CH₃)₂
 Formation: 5.3.2.6.1
- C₁₄H₁₆BNO**
 (C₆H₅)₂BO(CH₂)₂NH₂
 Formation: 5.3.2.4.2
- C₁₄H₁₈Be**
 (C₇H₉)₂Be
 Formation: 5.4.3.3.1
- C₁₄H₁₈Mg**
 Mg[CHCH=CH(CH₂)₂CH=CH]₂
 Formation: 5.4.2.3.1
- C₁₄H₁₉B**
 9-C₆H₅B-bicyclo[3.3.1]C₈H₁₄
 Formation: 5.3.2.4.3
- C₁₄H₂₀MgN₂**
 (C₂H₅)₂Mg·2 NC₅H₅
 Formation: 5.4.2.3.2
- C₁₄H₂₃Al**
 (i-C₄H₉)₂AlC₆H₅
 Formation: 5.3.3.5.4
- C₁₄H₂₃B**
 9-(C-C₆H₉)B-bicyclo[3.3.1]C₈H₁₄
 Formation: 5.3.2.5.1
- C₁₄H₂₃BO**
 n-C₄H₉(C₆H₅)BOC₄H₉-n
 Formation: 5.3.2.4.2
- C₁₄H₂₃BO₂**
 (i-C₄H₉O)₂BC₆H₅
 Formation: 5.3.2.4, 5.3.2.4.2
 Reaction with LiR: 5.3.2.4.2
- C₁₄H₂₆BeO₂**
 (CH₂=CHCH₂)₂Be·2 OC₄H₉
 Formation: 5.4.3.4.4
- C₁₄H₂₈B₁₀O₂**
 (C₆H₁₁)₂B₁₀H₆(CO)₂
 Formation: 5.3.2.7.5
- C₁₄H₂₉Al**
 (i-C₄H₉)₂AlCH=CHC₄H₉-i
 Reaction with CH₂N₂: 5.3.3.5.5

C₁₄H₂₉Al, *contd*

(i-C₄H₉)₂AlCH₂ $\overline{\text{CH}(\text{CH}_2)_3\text{CH}_2}$
 Formation, intramolecular carbalumination: 5.3.3.5.1

C₁₄H₂₉BrMgOSi

(CH₃)₃C(CH₃)₂SiOCH(C₂H₅)CH(CH₃)*
 CH=C(CH₃)MgBr
 Formation: 5.4.2.3.1

C₁₄H₂₉LiOSi

(CH₃)₃C(CH₃)₂SiOCH(C₂H₅)CH(CH₃)*
 CH=C(CH₃)Li
 Reaction with MgX₂: 5.4.2.3.1

C₁₄H₃₀Al₂Na₂

Na₂[(C₂H₅)₃AlC≡CAl(C₂H₅)₃]
 Formation: 5.3.3.5.2
 Reaction with Et₂AlCl: 5.3.3.3.2

C₁₄H₃₀Al₆

(CH₃)₆Al₆C₄(CH₃)₄
 Formation: 5.3.3.4.1

C₁₄H₃₀Be₂N₂

[CH₃BeC≡CCH₃·N(CH₃)₃]₂
 Formation: 5.4.3.4.4

C₁₄H₃₁Ga

(C₂H₅)₂GaC₁₀H₂₁-n
 Formation: 5.3.4.4.1
 Redistribution: 5.3.4.5.2

C₁₄H₃₂BLiSi₂

Li[C₈H₁₄B[Si(CH₃)₃]₂]
 Formation: 5.3.7.4.2, 5.3.7.4.3

C₁₄H₃₄MgO₂Si₂

Mg[Si(CH₃)₃]₂·2 $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$
 Formation: 5.4.4.4

C₁₄H₃₈AlClSi₄

{[(CH₃)₃Si]₂CH₂}₂AlCl
 Formation: 5.3.3.3.1

C₁₄H₃₈Ge₂MgO₄

Mg[Me₃Ge]₂·2 MeOCH₂CH₂OMe
 Formation: 5.4.5.5

C₁₄H₄₂Al₂N₂P₂Si

(CH₃)₂Si[N=P(CH₃)₃]₂[Al(CH₃)₃]₂
 Formation: 5.3.3.5.4

C₁₅H₁₁BIMnO₃

h⁵-CH₃C₅H₃BC₆H₅IMn(CO)₃
 Formation: 5.3.2.3.3

C₁₅H₁₅CaI

[C₂H₅(C₆H₅)₂C]CaI
 Formation from Ph₂C=CH₂: 5.4.3.4.1

C₁₅H₁₅In

(h¹-C₅H₅)₃In
 Formation: 5.3.5.3.1, 5.3.5.3.2

C₁₅H₁₅Tl

(h⁵-C₅H₅)₃Tl
 Formation: 5.3.6.2.6

C₁₅H₂₂BeN₂O

CH₃BeOC(CH₃)₃·2 NC₅H₅
 Formation: 5.4.3.3.2

C₁₅H₂₅B

9-[(CH₃)₂C=CCHCH(CH₃)]B-bicyclo[3.3.1]C₈H₁₄
 Formation: 5.3.2.5.1

C₁₅H₂₅BO

2-{bicyclo[2.2.1]C₇H₁₁}₂BOCH₃
 Formation: 5.3.2.5.1

C₁₅H₂₇B

(cyclo-C₅H₉)₃B
 Reaction with H₃B·THF: 5.3.2.5.3

C₁₅H₃₀B₂

[c-(CH₂)₅B]₂(CH₂)₅
 [(CH₂)₅B]₂CH(CH₂)₃CH₃
 Formation: 5.3.2.5.1, 5.3.2.6.1

C₁₅H₃₁Al

(i-C₄H₉)₂AlCH₂CH=CHC₄H₉-i
 Formation: 5.3.3.5.5

C₁₅H₃₃Al

[(CH₃)₃CCH₂]₃Al
 Decomposition: 5.3.3.5.3
 (n-C₅H₁₁)₃Al
 Formation: 5.3.3.2.2
 Racemisation: 5.3.3.2.3, 5.3.3.5.3

C₁₅H₃₃B

[(CH₃)₃CCH₂]₃B
 Reaction with BeR₂: 5.4.3.4.4

C₁₅H₃₃ClMgPb

[(CH₃)₃CCH₂]₃PbMgCl
 Formation: 5.4.7.2.5

C₁₅H₃₃Ga

(n-C₅H₁₁)₃Ga
 Formation: 5.3.4.2.2

C₁₅H₃₆AlLiSn

Li[(n-C₄H₉)₃SnAl(CH₃)₃]
 Formation: 5.3.18.3

C₁₅H₃₆B₂Si

[(CH₃)₃C]₂BB[C(CH₃)₃Si(CH₃)₃]
 Formation: 5.3.7.4.3

C₁₅H₃₆Be₃

[CH₃BeC(CH₃)₃]₃
 Formation: 5.4.3.4.4

C₁₅H₃₉AlSi₃

(CH₃)₃SiCH₂CH₂Al[CH(CH₃)Si(CH₃)₃]₂
 Formation: 5.3.3.2.1
 [(CH₃)₃SiC₂H₄]₃Al
 Formation: 5.3.3.4.1

C₁₆H₁₀

C₆H₅C≡CC≡CC₆H₅
 Reaction with R₂AlCl and Li metal:
 5.3.3.3.4

- C₁₆H₁₀B₄Co₂Sn**
[h⁵-C₅H₅CoC₂B₂C]₂Sn
Formation: 5.3.17.3.3
- C₁₆H₁₀Be**
(C₆H₅C≡C)₂Be
Formation by metallation: 5.4.3.4.2
- C₁₆H₁₀Ca**
Ca[C≡CC₆H₅]₂
Reaction with cyclopentadiene: 5.4.3.4.2
- C₁₆H₁₀Hg**
(C₆H₅C≡C)₂Hg
Reaction with Al metal: 5.3.3.2.3
- C₁₆H₁₂AlNaO₄**
Na[(OCH=CHCH=C)₄Al]
Formation: 5.3.3.5.2
- C₁₆H₁₂AlNaS₄**
Na[(SCH=CHCH=C)₄Al]
Formation: 5.3.3.5.2
- C₁₆H₁₂MgN₂**
[C₆H₅CH(CN)]₂Mg
Formation: 5.4.2.2.5
- C₁₆H₁₂S₄Sn**
(CHCHCHSC)₄Sn
Reaction with BX₃: 5.3.2.3.1
- C₁₆H₁₄BFel**
h⁵-C₅H₅FeC₃H₄BC₆H₅I-h⁵
Formation: 5.3.2.3.3
- C₁₆H₁₅BCo**
h⁵-C₅H₅Co(h⁵-C₅H₅BC₆H₅)
Formation by ring expansion: 5.3.2.3.4
- C₁₆H₁₅BrMg**
(C₆H₅)₂CCH₂C(CH₃)MgBr
Formation: 5.4.2.3.1
(C₆H₅)₂CC(MgBr)(CH₃)CH₂
Formation: 5.4.2.2.1
(C₆H₅)₂C(MgBr)CHCH₂CH₂
Formation and rearrangement: 5.4.2.3.1
- C₁₆H₁₅BrMgSn**
C₆H₅(C₅H₅)₂SnMgBr
Formation: 5.4.6.6
- C₁₆H₁₅Li**
(C₆H₅)₂CCH₂CCH₃Li
Reaction with MgX₂: 5.4.2.3.1
- C₁₆H₁₆BaN**
(C₆H₅C≡C)₂Ba·2 NH₃
Formation: 5.4.3.2.3
- C₁₆H₁₆CaN**
(C₆H₅C≡C)₂Ca·2 NH₃
Formation: 5.4.3.2.3
- C₁₆H₁₆Cl₂Mg₂**
C₆H₅CH(MgCl)CH₂CH₂CH(MgCl)C₆H₅
Formation from MgCl₂: 5.4.2.3.1
- C₁₆H₁₆Mg**
C₆H₅CHCH₂CH₂CH(C₆H₅)Mg
Formation: 5.4.2.2.4
[(C₆H₅)CHCH₂CH₂CH(C₆H₅)]Mg
Formation: 5.4.2.3.3
- C₁₆H₁₆NSr**
(C₆H₅C≡C)₂Sr·2 NH₃
Formation: 5.4.3.2.3
- C₁₆H₁₆Na₂**
C₆H₅CH(Na)CH₂CH₂CH(Na)C₆H₅
Reaction with MgX₂: 5.4.2.3.1
- C₁₆H₁₈BF₄O₂Tl**
[(4-C₂H₅OC₆H₄)₂Tl][BF₄]
Formation: 5.3.6.2.5
- C₁₆H₁₈BF₄Tl**
[(4-C₂H₅C₆H₄)₂Tl][BF₄]
Formation: 5.3.6.2.5
- C₁₆H₁₈Be**
[2,5-C₆H₃(CH₃)₂]₂Be
Formation: 5.4.3.4.4
- C₁₆H₁₉BO**
i-C₄H₉OB(C₆H₅)₂
Formation: 5.3.2.4.2
- C₁₆H₂₂BNO**
n-C₄H₉O(C₆H₅)₂B·NH₃
Formation: 5.3.2.4.2
Reaction with HO(CH₂)₂NH₂: 5.3.2.4.2
- C₁₆H₂₂Be**
(C₈H₁₁)₂Be
Formation: 5.4.3.3.1
- C₁₆H₂₂HgSi₂**
Hg[Si(CH₃)₂C₆H₅]₂
Reaction with Mg metal: 5.4.4.4
- C₁₆H₂₂Mg**
Mg[CHCH=CH(CH₂)₃CH=CH]₂
Formation: 5.4.2.3.1
- C₁₆H₂₂MgSi₂**
Mg[Si(CH₃)₂C₆H₅]₂
Attempted preparation: 5.4.4.4
- C₁₆H₂₄Al₂Be**
Be(μ-C≡CCH₃)₄[Al(CH₃)₂]₂
Formation: 5.4.3.4.4
- C₁₆H₂₅BO₂**
CH₂=C(C₆H₅)B[O(CH₂)₃CH₃]₂
Formation: 5.3.2.4.1
- C₁₆H₂₇B**
9-(c-C₆H₉-CH₂CH₂B)bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.5.1
- C₁₆H₂₈B₄**
(CH₃)₈C₈B₄H₄
Formation: 5.3.2.7.3
- C₁₆H₂₉B**
9-cyclo-C₈H₁₅B-bicyclo[3.3.1]C₈H₁₄
Formation: 5.3.2.6.3

- C₁₆H₃₀B₂**
 {9-HB-bicyclo[3.3.1]C₈H₁₄}₂
 Formation: 5.3.2.5.1
 Hydroboration mechanism: 5.3.2.5.1
 Reaction with Li[R₃Si]: 5.3.7.4.2
- C₁₆H₃₀Mg**
 [(CH₃)₃CCH₂CH=CHCH₂]₂Mg
 Formation: 5.4.2.3.1
- C₁₆H₃₁B**
 2-{4,8-(CH₃)₂-bicyclo[3.3.1]C₈H₁₀}B-C*
 (CH₃)₂CH(CH₃)₂
 Formation: 5.3.2.5.1
- C₁₆H₃₂Li**
 Li{9[CH₃(CH₂)₃]₂B-bicyclo-
 [3.3.1]C₈H₁₄}
 Formation: 5.3.2.5.2
- C₁₆H₃₆GaLi**
 Li[(n-C₄H₉)₄Ga]
 Formation: 5.3.4.3.1
- C₁₆H₃₆O₄Ti**
 Ti(OC₄H₉-n)₄
 Catalyst for hydroalumination of un-
 dec-5-ene: 5.3.3.4.1
- C₁₆H₃₇AlO**
 (t-C₄H₉)₃Al·O(C₂H₅)₂
 Formation: 5.3.3.3.1
 Reaction with C₂H₄: 5.3.3.5.1
 Thermal decomposition, ether cleavage:
 5.3.3.5.3
- C₁₆H₃₇AlSn**
 (n-C₄H₉)₃SnAl(C₂H₅)₂
 Formation: 5.3.18.3
- C₁₆H₃₈B₂**
 [CH₃(CH₂)₃]₂BH₂B[(CH₂)₃CH₃]₂
 Redistribution: 5.3.2.5.3
- C₁₆H₃₈B₂N₂**
 (CH₃)₂N(CH₂)₂N(CH₃)₂·2(H₂B-c-C₅H₉)
 Formation: 5.3.2.5.1
- C₁₆H₃₈Be₂K₂O₂**
 [KBe(C₂H₅)₂·OC(CH₃)₃]₂
 Formation: 5.4.3.4.2
- C₁₆H₄₀AlGaLi₂**
 LiAl(C₂H₅)₄·LiGa(C₂H₅)₄
 Li(7) and H NMR: 5.3.4.5.2
- C₁₆H₄₀AlSb**
 [(C₂H₅)₄Sb][(C₂H₅)₄Al]
 Formation: 5.3.3.5.4
- C₁₆H₄₀Al₂Ba**
 Ba[Al(C₂H₅)₄]₂
 Formation: 5.4.3.3.1
 Reaction with PhC≡CH: 5.4.3.4.2
- C₁₆H₄₀Al₂Ca**
 Ca[Al(C₂H₅)₄]₂
 Formation: 5.4.3.3.1
 Reaction with PhC≡CH: 5.4.3.4.2
 Reaction with indene: 5.4.3.4.2
- C₁₆H₄₀Al₂Sr**
 Sr[Al(C₂H₅)₄]₂
 Formation: 5.4.3.3.1
 Reaction with PhC≡CH: 5.4.3.4.2
- C₁₆H₄₀Be₄S₄**
 (C₂H₅BeSC₂H₅)₄
 Formation: 5.4.3.3.2
- C₁₆H₄₂B₂N₂**
 (CH₃)₂N(CH₂)₂N(CH₃)₂·2 H₂B(CH₃)*
 CH₃CH(CH₃)₂
 Formation: 5.3.2.5.1
- C₁₆H₄₂Be₂N₂**
 [C₅H₁₁BeH·N(CH₃)₃]₂
 Formation from 1-pentene: 5.4.3.4.3
- C₁₆I₄K₂Mg**
 C₁₆Mg(KI)₂
 Formation: 5.4.2.3.1
- C₁₇H₁₈BrMgSi**
 CH₃(C₆H₅)(1-C₁₀H₇)SiMgBr
 Formation: 5.4.4.5
- C₁₇H₁₅ClGeMg**
 (1-C₁₀H₇)(C₆H₅)CH₃GeMgCl
 Formation: 5.4.5.3
- C₁₇H₁₆BN**
 (C₆H₅)₂HB·NC₅H₅
 Formation: 5.3.2.5.1
- C₁₇H₁₆Ge**
 (1-C₁₀H₇)(C₆H₅)CH₃GeH
 Reaction with RMgX: 5.4.5.3
- C₁₇H₁₉Al**
 (CH₃)₂Al(C₆H₅)C=C(C₆H₅)CH₃
 Formation: 5.3.3.5.1
- C₁₇H₂₂BrMgSi**
 (CH₃)₂CH₂CH₂CH(MgBr)SiH(C₆H₅)₂
 Formation: 5.4.2.5.1
- C₁₇H₂₅BO₂**
 CH₂=C=C(C₆H₅)B[O(CH₂)₃CH₃]₂
 Formation: 5.3.2.4.1
 C₆H₅C≡CCH₂B[O(CH₂)₃CH₃]₂
 Formation: 5.3.2.4.1
- C₁₇H₂₇AlCa**
 [(Indenyl)Ca][Al(C₂H₅)₄]
 Formation: 5.4.3.4.2
- C₁₇H₄₂Ga₂N₂**
 [(CH₃)₄N][[(C₂H₅)₃Ga]₂CN]
 Formation: 5.3.4.5.3
- C₁₈BrF₁₅MgPb**
 (C₆F₅)₃PbMgBr
 Formation: 5.4.7.2.5

- C₁₈F₁₅In**
(C₆F₅)₃In
Formation: 5.3.5.2.5, 5.3.5.2.6, 5.3.5.2.1, 5.3.5.3.1
- C₁₈F₁₅Tl**
(C₆F₅)₃Tl
Formation: 5.3.6.3.9
- C₁₈HF₁₅Ge**
(C₆F₅)₃GeH
Reaction with TlR₃: 5.3.16
- C₁₈H₃F₁₂Tl**
(3-HC₆F₄)₃Tl
Formation: 5.3.6.3.9
- C₁₈H₁₂BCl₃**
(4-ClC₆H₄)₃B
Reaction with BeR₂: 5.4.3.4.4
- C₁₈H₁₂Br₃Ga**
(3-BrC₆H₄)₃Ga
Formation: 5.3.4.2.3
(4-BrC₆H₄)₃Ga
Formation: 5.3.4.2.3
- C₁₈H₁₂Br₃In**
(4-BrC₆H₄)₃In
Formation: 5.3.5.3.1
- C₁₈H₁₂Cl₃Ga**
(2-ClC₆H₄)₃Ga
Formation: 5.3.4.2.3
(3-ClC₆H₄)₃Ga
Formation: 5.3.4.2.3
(4-ClC₆H₄)₃Ga
Formation: 5.3.4.2.3
- C₁₈H₁₂Cl₃In**
(4-ClC₆H₄)₃In
Formation: 5.3.5.2.5
- C₁₈H₁₂F₃Ga**
(3-FC₆H₄)₃Ga
Formation: 5.3.4.2.3
(4-FC₆H₄)₃Ga
Formation: 5.3.4.2.3
- C₁₈H₁₂F₃In**
(3-FC₆H₄)₃In
Formation: 5.3.5.2.5
(4-FC₆H₄)₃In
Formation: 5.3.5.2.5
- C₁₈H₁₃Al**
(o-C₆H₄-Al-C₆H₄-o)C₆H₅
Formation, cyclization: 5.3.3.5.2
- C₁₈H₁₄Ca**
(Indenyl)₂Ca
Formation: 5.4.3.2.3
- C₁₈H₁₄Mg**
(C₆H₇)₂Mg
Formation: 5.4.2.3.2
- C₁₈H₁₅Al**
(C₆H₅)₃Al
Alumination of alkynes: 5.3.3.5.2
Formation: 5.3.3.2.3, 5.3.3.3.1, 5.3.3.3.2, 5.3.3.3.4
Reaction with o-C₆H₅C₆H₄NHCH₃: 5.3.3.5.2
Reaction with Ph₂CN₂: 5.3.3.5.5
Reaction with Na[R₄Al]: 5.3.3.5.4
Reaction with dienes: 5.3.3.5.1
Reactivity towards olefins: 5.3.3.5.1
Thermal decomposition, cyclization: 5.3.3.5.2
- C₁₈H₁₅Al₂Br₃**
(C₆H₅)₃Al₂Br₃
Formation: 5.3.3.2.2
- C₁₈H₁₅Al₂Cl₃**
(C₆H₅)₃Al₂Cl₃
Formation: 5.3.3.2.2
Reaction with R₃Al: 5.3.3.3.2
Reaction with Na metal: 5.3.3.3.4
- C₁₈H₁₅Al₂I₃**
(C₆H₅)₃Al₂I₃
Formation: 5.3.3.2.2
- C₁₈H₁₅B**
(C₆H₅)₃B
Exchange with R₃Al: 5.3.3.5.4
Reaction with boron—nitrogen bonds: 5.3.2.6.1
Reaction with Li[R₃Si]: 5.3.7.4.2
Reaction with BeR₂: 5.4.3.4.4
- C₁₈H₁₅B₃Cl₃N₃**
(C₆H₅)₃N₃B₃Cl₃
Reactions with K[R₃Si]: 5.3.7.4.1
- C₁₈H₁₅B₃O₆**
(2-HOC₆H₄BO)₃
Formation: 5.3.2.4.1
- C₁₈H₁₅BeLi**
LiBe(C₆H₅)₃
Formation: 5.4.3.4.4
- C₁₈H₁₅BrGeMg**
(C₆H₅)₃GeMgBr
Formation: 5.4.5.2, 5.4.5.4
- C₁₈H₁₅BrMgPb**
(C₆H₅)₃PbMgBr
Formation: 5.4.7.2.2, 5.4.7.2.5
- C₁₈H₁₅BrMgSi**
(C₆H₅)₃SiMgBr
Formation: 5.4.4.5
Formation as an intermediate: 5.4.4.2

- C₁₈H₁₅BrMgSn**
(C₆H₅)₂Sn·C₆H₅MgBr
Formation: 5.4.6.6
- C₁₈H₁₅ClGe**
(C₆H₅)₃GeCl
Reaction with Mg metal: 5.4.5.2
- C₁₈H₁₅ClGeMg**
(C₆H₅)₃GeMgCl
Formation: 5.4.5.3
- C₁₈H₁₅ClMgPb**
(C₆H₅)₃PbMgCl
Formation: 5.4.7.2.5
- C₁₈H₁₅ClSi**
(C₆H₅)₃SiCl
Reaction with RMgX: 5.4.4.2
Reaction with (R₂N)₂BX: 5.3.7.3.1
- C₁₈H₁₅ClSn**
(C₆H₅)₃SnCl
Reaction with Mg metal: 5.4.6.2
- C₁₈H₁₅DGe**
(C₆H₅)₃GeD
Formation: 5.4.5.2, 5.4.5.4
Reaction with RMgX: 5.4.5.3
- C₁₈H₁₅Ga**
(C₆H₅)₃Ga
Formation: 5.3.4.2.3
- C₁₈H₁₅GeK**
K[(C₆H₅)₃Ge]
Reaction with chloroborazines:
5.3.12.2.1
- C₁₈H₁₅GeLi**
Li[(C₆H₅)₃Ge]
Reaction with Li[AlH₄]: 5.3.13.3
- C₁₈H₁₅In**
(C₆H₅)₃In
Formation: 5.3.5.2.5, 5.3.5.3.1
Reaction with InX₃: 5.3.5.3.2
- C₁₈H₁₅KSi**
K[(C₆H₅)₃Si]
Reaction with AlX₃: 5.3.8.2.1
Reaction with (CH₃)₃N₃B₃Cl₃: 5.3.7.4.1
Reaction with (C₆H₅)₃N₃B₃Cl₃:
5.3.7.4.1
- C₁₈H₁₅LiSi**
(C₆H₅)₃SiLi
Reaction with (R₂N)₂BX: 5.3.7.4.1
(C₆H₅)₃SiLi
Reaction with LiAlH₄ and AlH₃:
5.3.8.2.2
Reaction with Et₂AlX: 5.3.8.2.1
- C₁₈H₁₅LiSi**
Li[(C₆H₅)₃Si]
Reaction with R₃B: 5.3.7.4.2
- Reaction with (CH₃)₃N₃B₃Cl₃: 5.3.7.4.1
- C₁₈H₁₅Tl**
(C₆H₅)₃Tl
Formation: 5.3.6.2.1, 5.3.6.3.2
Reaction with RLi: 5.3.6.4.2
- C₁₈H₁₆Ge**
(C₆H₅)₃GeH
Formation: 5.4.5.4
Reaction with RMgX: 5.4.5.3
- C₁₈H₁₆Sn**
(C₆H₅)₃SnH
Formation: 5.4.6.2, 5.4.6.3
Reaction with RMgBr·NR₃: 5.4.6.5
Reaction with TIR₃: 5.3.21.1
- C₁₈H₁₈AlGeLi**
Li[(C₆H₅)₃GeAlH₃]
Formation: 5.3.13.3, 5.3.13.4
- C₁₈H₁₈AlLiSi**
Li[(C₆H₅)₃SiAlH₃]
Formation: 5.3.8.2.2, 5.3.8.7
- C₁₈H₁₉BrMgSn**
C₆H₅(H₃CC₅H₄)₂SnMgBr
Formation: 5.4.6.6
- C₁₈H₂₁In**
(h¹-CH₃C₅H₄)₃In
Formation: 5.3.5.3.1
- C₁₈H₂₂Be**
[2,4,6-C₆H₂(CH₃)₃]₂Be
Formation: 5.4.3.3.1
- C₁₈H₂₂Mg**
[2,4,6-(CH₃)₃C₆H₂]₂Mg
Formation: 5.4.2.3.2
- C₁₈H₂₆AlClZr**
n-C₃H₇(CH₃)C=C[Al(CH₃)₂]₂Zr(C₅H₅-h⁵)₂Cl
Formation: 5.3.3.5.1
- C₁₈H₂₆CaO₂**
(C₂H₅)₂Ca·2 $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$
Formation: 5.4.3.2.3
- C₁₈H₂₇Ga**
(n-C₄H₉C≡C)₃Ga
Formation: 5.3.4.5.1
- C₁₈H₂₈MgN₂**
(t-C₄H₉)Mg·2 NC₅H₅
Formation: 5.4.2.3.2
- C₁₈H₃₀B₂**
{2-HB-tricyclo[3.3.1.1^{3,7}]₂C₉H₁₄}₂
Formation: 5.3.2.5.1
- C₁₈H₃₀Be₂N₂**
[(CH₃C≡C)₂Be·N(CH₃)₃]₂
Redistribution with BeR₂: 5.4.3.4.4
- C₁₈H₃₃B**
B(C₂H₅C=CHC₂H₅)₃
Formation: 5.3.2.5.1

- (cyclo- C_6H_{11})₂BCH=CH(CH₂)₃CH₃
Formation: 5.3.2.5.1
- C₁₈H₃₃B₃O₆**
(c- C_6H_{11} OBO)₃
Reaction with RMgX: 5.3.2.4.2
- C₁₈H₃₃Ga**
[CH₂=CH(CH₂)₄]₃Ga
Formation: 5.3.4.2.3
(cyclo- C_5H_9 CH₂)₃Ga
Formation: 5.3.4.2.3
- C₁₈H₃₃In**
[(CH₂)₄CH=CH₂]₃In
Formation: 5.3.5.2.5
(cyclo- C_5H_9 CH₂)₃In
Formation: 5.3.5.2.5
- C₁₈H₃₅BO**
(CH₃)₂CHC(CH₃)₂B(OCH₃)(n- C_3H_7 C*
H=CH)C=CH(C_4H_9 -n)
Formation: 5.3.2.5.1
- C₁₈H₃₇B**
n- C_9H_{19} B(CH₂)₄CHC₄H₉-n
Formation: 5.3.2.6.3
- C₁₈H₃₉Al**
[(CH₃)₃CCH₂CH₂]₃Al
Formation: 5.3.3.5.1
(n- C_6H_{13})₃Al
Formation: 5.3.3.2.2
- C₁₈H₄₂AlLiSn**
Li[(n- C_4H_9)₃SnAl(C_2H_5)₃]
Formation: 5.3.18.3
- C₁₈H₄₂B₂N₂**
(CH₃)₂N(CH₂)₂N(CH₃)₂·2(H₂B-c- C_6H_{11})
Formation: 5.3.2.5.1
- C₁₈H₄₂Sn₂**
(n- C_3H_7)₃SnSn(C_3H_7 -n)₃
Reaction with RMgX: 5.4.6.4
- C₁₈H₄₅GaGe₃**
Ga[(C_2H_5)₃Ge]₃
Possible formation: 5.3.14
- C₁₈H₄₅Ge₃In**
In[(C_2H_5)₃Ge]₃
Possible formation: 5.3.15
- C₁₈H₄₅Ge₃Tl**
Tl[(C_2H_5)₃Ge]₃
Formation: 5.3.16
Reaction with R₃SnH: 5.3.21.1
- C₁₈H₄₅Si₃Tl**
Tl[Si(C_2H_5)₃]₃
Formation: 5.3.11.1
- C₁₈H₄₅Sn₃Tl**
[(C_2H_5)₃Sn]₃Tl
Attempted preparation: 5.3.21.1
- C₁₈H₄₈AlClOSi₄**
{[(CH₃)₃Si]₂CH₂}₂ClAl·O(C_2H_5)₂
Formation: 5.3.3.3.1
- C₁₈H₅₄AlPSi₆**
[(CH₃)₃Si]₃AlP[Si(CH₃)₃]₃
Formation: 5.3.8.3
- C₁₉H₁₃BrMg**
 C_6H_5 (C_6H_4 C_6H_4)CMgBr
Formation: 5.4.2.3.3
- C₁₉H₁₃IMg**
 C_6H_5 (C_6H_4 C_6H_4)CMgI
Formation: 5.4.2.3.3
- C₁₉H₁₅**
(C_6H_5)₃C·
Reaction with Mg metal: 5.4.2.2.3
- C₁₉H₁₅BaCl**
[(C_6H_5)₃C]BaCl
Polymerization: 5.4.3.4.1
- C₁₉H₁₅BrMg**
(C_6H_5)₃CMgBr
Formation: 5.4.2.3.1, 5.4.2.3.3
- C₁₉H₁₅CaCl**
[(C_6H_5)₃C]CaCl
Metallation of RH: 5.4.3.4.2
- C₁₉H₁₅CaI**
[(C_6H_5)₃C]CaI
Formation: 5.4.3.4.2
- C₁₉H₁₅IMg**
(C_6H_5)₃CMgI
Formation: 5.4.2.3.3
- C₁₉H₁₅Na**
Na[C(C_6H_5)₃]
Reaction with MgX₂: 5.4.2.3.1
- C₁₉H₁₆GeO₂**
(C_6H_5)₃GeCOOH
Formation: 5.4.5.3
- C₁₉H₂₅Mg**
 C_9H_7 Mg[CH₂CH=CH(CH₃)(CH₂)₂C*
H=C(CH₃)₂]
Reaction with MgX₂: 5.4.2.3.2
- C₁₉H₄₃AlO**
[(CH₃)₂CHCH₂CH₂]₃Al·O(C_2H_5)₂
Formation: 5.3.3.5.1
- C₂₀H₁₃IMg**
HC(1,2- C_6H_4)₃CMgI
Formation: 5.4.2.3.1
- C₂₀H₁₃Li**
HC(1,2- C_6H_4)₃CLi
Reaction with MgX₂: 5.4.2.3.1
- C₂₀H₁₄Be**
(1-naphthyl)₂Be
Formation: 5.4.3.4.4

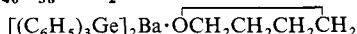
- C₂₀H₁₄BrIn**
(1-naphthyl)₂InBr
Formation: 5.3.5.3.1
- C₂₀H₁₄Hg**
(1-C₁₀H₇)₂Hg
Reaction with Ca metal: 5.4.3.2.2
- C₂₀H₁₅Al**
(C₆H₅)₂AlC≡CC₆H₅
Intramolecular carbalumination:
5.3.3.5.1
- C₂₀H₁₅BO**
(1-C₁₀H₇)₂BOH
Formation: 5.3.2.4.2
- C₂₀H₂₀BeO**
(C₆H₅C≡C)₂Be·O(C₂H₅)₂
Formation: 5.4.3.3.1
- C₂₀H₂₁SnTl**
(CH₃)₂TlSn(C₆H₅)₃
Formation: 5.3.21.1
- C₂₀H₂₂Ga₂**
[(CH₃)₂GaC≡CC₆H₅]₂
Formation: 5.3.4.5.1
- C₂₀H₂₂In₂**
[C₆H₅C≡CIn(CH₃)₂]₂
Formation: 5.3.5.4.2
- C₂₀H₂₅Al**
(C₂H₅)₂Al(C₆H₅)C=C(C₆H₅)C₂H₅
Formation: 5.3.3.5.1
- C₂₀H₂₆CaO₂**
(C₆H₅)₂Ca·2 OC₄H₈
Formation: 5.4.3.2.2
- C₂₀H₂₆Mg**
[C₆H₅(CH₃)₂CCH₂]₂Mg
Formation: 5.4.2.3.2
- C₂₀H₂₈BLiO₂**
Li[(C₆H₅)₂B(OC₄H₉-i)₂]
Formation: 5.3.2.4.2
- C₂₀H₃₀BeO₂**
(C₆H₅)₂Be·2 O(C₂H₅)₂
Formation: 5.4.3.3.1
- C₂₀H₃₅B**
{2,6,6-(CH₃)3-bicyclo[3.1.1]C₇H₈}₂BH
Formation: 5.3.2.5.1
Hydroborating agent: 5.3.2.5.1
- C₂₀H₃₈B₂Si**
[CH₃CB(CH₃)C[C(CH₃)₃]CH₂CH₂]₂Sn
Formation: 5.3.17.3.3
- C₂₀H₄₂B₂N₂**
{bicyclo[2.2.1]C₇H₁₁-BH₂}₂·(CH₃)₂N(C*H₂)₂N(CH₃)₂
Formation: 5.3.2.5.1
- C₂₀H₄₂Be₂N₂**
[CH₃BeC≡CCMe₃·N(CH₃)₃]₂
Formation: 5.4.3.4.4
- C₂₀H₄₆B₂**
{[(CH₃)₂CHCHCH₃]₂BH}₂
Hydroboration reagent: 5.3.2.5.1
- C₂₀H₄₆B₂N₂**
[2-CH₃-c-C₆H₁₀-BH₂]₂·(CH₃)₂N(CH₂)₂·N(CH₃)₂
Formation: 5.3.2.5.1
- C₂₀H₄₆Be₂Li₂O₄**
{LiBe(C₂H₅)[OC(CH₃)₃]₂]₂
Formation: 5.4.3.3.1
- C₂₀H₄₈Be₄O₄**
{CH₃Be[OC(CH₃)₃]}₄
Formation: 5.4.3.3.2
- C₂₁H₉F₁₂O₃Tl**
(3-CH₃OC₆F₄)₃Tl
Formation: 5.3.6.3.9
- C₂₁H₁₅CoO₄Si**
(CO)₄CoSi(CH₃)C₆H₅(α-C₁₀H₇)
Reaction with RMgX: 5.4.4.5
- C₂₁H₂₁Al**
(C₆H₅CH₂)₃Al
Formation: 5.3.3.2.3, 5.3.3.5.4
Reaction with diphenylacetylene:
5.3.3.5.1
(p-CH₃C₆H₄)₃Al
Transmetallation: 5.3.3.5.4
- C₂₁H₂₁B**
(C₆H₅CH₂)₃B
Exchange with R₃Al: 5.3.3.5.4
(2-C₆H₄CH₃)₃B
Reaction with BeR₂: 5.4.3.4.4
(3-C₆H₄CH₃)₃B
Reaction with BeR₂: 5.4.3.4.4
- C₂₁H₂₁BeLi**
LiBe(2-C₆H₄CH₃)₃
Formation: 5.4.3.4.4
- C₂₁H₂₁Ga**
(2-CH₃C₆H₄)₃Ga
Formation: 5.3.4.2.3
(3-CH₃C₆H₄)₃Ga
Formation: 5.3.4.2.3
(4-CH₃C₆H₄)₃Ga
Formation: 5.3.4.2.3
- C₂₁H₂₁GaO**
(C₆H₅C≡C)₂CH₃Ga·O(CH₂)₄
Formation: 5.3.4.5.1
- C₂₁H₂₁GaO₃**
(4-CH₃OC₆H₄)₃Ga
Formation: 5.3.4.2.3
- C₂₁H₂₁In**
(C₆H₅CH₂)₃In
Formation: 5.3.5.3.3

- (2-CH₃C₆H₄)₃In
Formation: 5.3.5.2.5, 5.3.5.3.1
- (3-CH₃C₆H₄)₃In
Formation: 5.3.5.2.5
- (4-CH₃C₆H₄)₃In
Formation: 5.3.5.2.5, 5.3.5.3.1
- C₂₁H₂₁InO₃**
(4-CH₃OC₆H₄)₃In
Formation: 5.3.5.2.5
- C₂₁H₂₄Si₂**
(CH₃)₃SiSi(C₆H₅)₃
Formation: 5.4.4.2
- C₂₁H₂₈CaClO₂**
(Fluorenyl)CaCl·2 OC₄H₈
Formation: 5.4.3.4.2
- C₂₁H₃₃Al**
(C₇H₁₁)₃Al
Formation: 5.3.3.4.2
- C₂₁H₃₃B**
{2-bicyclo[2.2.1]C₇H₁₁}₃B
Reaction with H₃B·THF: 5.3.2.5.3
- C₂₁H₄₅Al**
(n-C₇H₁₅)₃Al
Formation: 5.3.3.2.2
- C₂₁H₅₇GaSi₆**
Ga{CH[Si(CH₃)₃]₂}₃
Formation: 5.3.4.3.1
- C₂₁H₅₇InSi₆**
{[(CH₃)₃Si]₂CH}₃In
Formation: 5.3.5.3.1
- C₂₂H₁₀F₁₅GaO**
(C₆F₅)₃Ga·O(C₂H₅)₂
Formation: 5.3.4.3.1
- C₂₂H₁₀F₁₅InO**
(C₆F₅)₃In·O(C₂H₅)₂
Formation: 5.3.5.2.1, 5.3.5.2.5
- C₂₂H₁₅CoGeO₄**
(CO)₄CoGe(C₆H₅)₃
Reaction with RMgX: 5.4.5.4
- C₂₂H₁₅CoO₄Si**
(CO)₄CoSi(C₆H₅)₃
Reaction with RMgX: 5.4.4.5
- C₂₂H₂₀MgN₂**
(C₆H₅)₂Mg·2 NC₅H₅
Formation: 5.4.2.3.2
- C₂₂H₂₄GeO**
(C₆H₅)₃Ge(CH₂)₄OH
Formation: 5.4.5.3
- C₂₂H₂₅AlO**
(C₆H₅)₃Al·O(C₂H₅)₂
Formation: 5.3.3.3.1
- C₂₂H₂₅AlSi**
(C₆H₅)₃SiAl(C₂H₅)₂
Formation: 5.3.8.2.1
- C₂₂H₂₅GeTi**
(C₆H₅)₃GeTi(C₂H₅)₂
Formation: 5.3.16
- C₂₂H₂₇BN₂Si**
(C₆H₅)₃SiB[N(CH₃)₂]₂
Formation: 5.3.7.3.1, 5.3.7.4.1
- C₂₂H₂₈Sn**
7,7-di-n-butyl-7-stannadibenzonorbornadiene
Formation: 5.4.2.2.4
- C₂₂H₃₀CaO₂**
(2-CH₃C₆H₄)₂Ca·2 OC₄H₈
Formation: 5.4.3.2.2
- (3-CH₃C₆H₄)₂Ca·2 OC₄H₈
Formation: 5.4.3.2.2
- (4-CH₃C₆H₄)₂Ca·2 OC₄H₈
Formation: 5.4.3.2.2
- C₂₂H₃₂Be₂**
[(o-C₆H₄CH₃)BeC(CH₃)₃]₂
Formation: 5.4.3.4.4
- C₂₂H₅₀Al₂N₂**
(C₂H₅)₂AlC≡Al(C₂H₅)₂·2 N(C₂H₅)₃
Formation: 5.3.3.5.2
- C₂₂H₅₅Al₂Sb**
[(C₂H₅)₄Sb][(C₂H₅)₇Al₂]
Formation: 5.3.3.5.4
- C₂₄H₁₉Al**
(C₆H₅)₂AlC₆H₄C₆H₅-o
Formation, cyclization: 5.3.3.5.2
Thermal decomposition, cyclization: 5.3.3.5.2
- C₂₄H₂₀AlLi**
Li[(C₆H₅)₄Al]
Reaction with MgH₂: 5.4.2.4.3
- C₂₄H₂₀AlNa**
Na[(C₆H₅)₄Al]
Formation: 5.3.3.5.2
- C₂₄H₂₀AsCl₃Sn**
[(C₆H₅)₄As][SnCl₃]
Reaction with BX₃: 5.3.17.4
- C₂₄H₂₀BNa**
Na[(C₆H₅)₄B]
Reaction with BF₃·OEt₂: 5.3.3.5.4
- C₂₄H₂₀Pb**
(C₆H₅)₄Pb
Formation: 5.4.7.2.2
Reaction with Ba, Sr, Ca and Li metals: 5.4.7.2.3
- C₂₄H₂₀Sn**
(C₆H₅)₄Sn
Exchange with M[ZnEt₄]: 5.4.3.4.4
Reaction with BX₃: 5.3.2.3.1

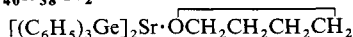
- C₂₄H₂₀Sn**, *contd*
Reaction with RBX₂: 5.3.2.3.1
- C₂₄H₂₆BeO₂**
(C₆H₅C≡C)₂Be·2 OC₄H₈
Reaction with LiC≡CPh: 5.4.3.4.4
- C₂₄H₂₇B**
[2,5-C₆H₃(CH₃)₂]₃B
Reaction with BeR₂: 5.4.3.4.4
- C₂₄H₂₇Ga**
(4-C₂H₅C₆H₄)₃Ga
Formation: 5.3.4.2.3
- C₂₄H₂₇In**
(4-C₂H₅C₆H₄)₃In
Formation: 5.3.5.2.5
- C₂₄H₂₉BSi**
CH₃(C₂H₅)₂CB(H)Si(C₆H₅)₃
Formation: 5.3.7.4.1
- C₂₄H₃₀BNSi**
(C₆H₅)₃SiB(C₄H₉)N(CH₃)₂
Formation: 5.3.7.4.1
- C₂₄H₃₀BrMgNSn**
(C₆H₅)₃SnMgBr·N(C₂H₅)₃
Formation: 5.4.6.5
- C₂₄H₃₆AlNa**
Na[(n-C₄H₉C≡C)₄Al]
Reaction with alkynes: 5.3.3.5.2
- C₂₄H₃₆Be₂**
[2,5-C₆H₃(CH₃)₂BeC(CH₃)₃]₂
Formation: 5.4.3.4.4
- C₂₄H₃₆GaK**
K[(n-C₄H₉C≡C)₄Ga]
Formation: 5.3.4.4.1
- C₂₄H₄₇B**
[CH₃(CH₂)₆CH=CH]₂B(CH₃)₂CCH(C*H₃)₂
Formation: 5.3.2.5.1
- C₂₄H₅₁Al**
(n-C₈H₁₇)₃Al
Formation: 5.3.3.2.2
- C₂₄H₅₁Al₂I₃**
(n-C₈H₁₇)₃Al₂I₃
Formation: 5.3.3.2.2
- C₂₄H₅₂GaNa**
Na[(n-C₆H₁₃)₄Ga]
Formation: 5.3.4.4.1
- C₂₄H₅₄Al₂**
(i-C₄H₉)₆Al₂
Reaction with InX₃: 5.3.5.3.1
- C₂₄H₅₄Be₃O₆**
{Be[OC(CH₃)₃]₂}₃
Reaction with BeMe₂: 5.4.3.3.2
- C₂₄H₅₄Sn₂**
(i-C₄H₉)₃SnSn(i-C₄H₉)₃
Reaction with RMgX: 5.4.6.4
- (n-C₄H₉)₃SnSn(n-C₄H₉)₃
Reaction with RMgX: 5.4.6.4
- C₂₄H₆₆AlKO₃Si₄**
K[Al[Si(CH₃)₃]₄]₃ O(C₂H₅)₂
Formation: 5.3.8.5
- C₂₄H₆₆AlLiO₃Si₄**
Li[Al[Si(CH₃)₃]₄]₃ O(C₂H₅)₂
Formation: 5.3.8.4
- C₂₄H₆₆GaLiO₃Si₄**
Li[Ga[Si(CH₃)₃]₄]₃ O(C₂H₅)₂
Formation: 5.3.9
- C₂₄H₇₀Al₂N₂Si₆**
[(CH₃)₃Si]₃Al·N(CH₃)₂CH₂CH₂(CH₃)₂*
N·Al[Si(CH₃)₃]₃
Formation: 5.3.8.3
- C₂₅H₂₂AlN**
(C₆H₅)₂AlNCH₃(C₆H₄C₆H₅-o)
Formation: 5.3.3.5.2
Thermal decomposition, cyclization: 5.3.3.5.2
- C₂₅H₂₂Pb**
(C₆H₅)₃PbCH₂C₆H₅
Formation: 5.4.7.2.1, 5.4.7.2.2
- C₂₆H₁₈Ba**
(Fluorenyl)₂Ba
Formation: 5.4.3.4.2
- C₂₆H₁₈Sr**
(Fluorenyl)₂Sr
Formation: 5.4.3.4.2
- C₂₆H₂₂Ca**
Ca[CH(C₆H₅)₂]₂
Formation: 5.4.3.4.2
- C₂₆H₂₆B₂Sn**
(CH₃)₂Sn[B(C₆H₅)₂]₂
Formation: 5.3.17.3.1
- C₂₆H₃₀CaO₂**
(Indenyl)₂Ca·2 OC₄H₈
Formation: 5.4.3.4.2
- C₂₆H₃₆GaPSi**
(C₂H₅)₂GaCH₂Si(CH₃)₃·P(C₆H₅)₃
Formation: 5.3.4.3.4
- C₂₆H₅₂AlNaSi₄**
Na[Al[Si(CH₃)₃]₄]₂·2 C₆H₅CH₃
Formation: 5.3.8.5
- C₂₆H₅₄Al₂Na₂**
Na₂[(i-C₄H₉)₃AlC≡CAl(C₄H₉-i)₃]
Formation: 5.3.3.5.2
- C₂₆H₅₄B₂N₂**
{2,6,6-(CH₃)₃-bicyclo-[3.1.1]C₇H₈-BH₂}₂*
(CH₃)₂N(CH₂)₂N(CH₃)₂
Formation: 5.3.2.5.1
- C₂₇H₂₁BrIn**
(Indenyl)₃In
Formation: 5.3.5.3.1

- C₂₇H₂₁Ga**
(indenyl)₃Ga
Formation: 5.3.4.2.3
- C₂₇H₂₁In**
(indenyl)₃In
Formation: 5.3.5.2.5
- C₂₇H₂₄AlN**
(C₆H₅C≡C)₃Al·N(CH₃)₃
Formation: 5.3.3.2.3
- C₂₇H₃₁CaClO₂**
(C₆H₅)₃CClCa·2 $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$
Formation and stability: 5.4.3.2.1
- C₂₇H₃₃Ga**
[2,4,6-(CH₃)₃C₆H₂]₃Ga
Formation: 5.3.4.2.3
- C₂₇H₅₇Al**
(n-C₉H₁₉)₃Al
Formation: 5.3.3.2.2
- C₂₇H₅₇In**
(n-C₉H₁₉)₃In
Formation: 5.3.5.3.1
- C₂₈H₂₀Li₂**
[(C₆H₅)₄C₄]₂Li₂
Reaction with PhAlCl₂: 5.3.3.3.1
- C₂₈H₂₄Ba**
Ba[C(C₆H₅)₂CH₂CH₂(C₆H₅)₂C]
Polymerization of dienes: 5.4.3.4.1
Polymerization of styrene: 5.4.3.4.1
Reaction with fluorene: 5.4.3.4.2
- C₂₈H₂₄Sr**
Sr[C(C₆H₅)₂CH₂CH₂(C₆H₅)₂C]
Polymerization of dienes: 5.4.3.4.1
Reaction with fluorene: 5.4.3.4.2
- C₂₈H₂₅AlO**
(C₆H₅C≡C)₃Al·O(C₂H₅)₂
Formation: 5.3.3.2.3
- C₂₈H₃₀CaO₂**
(i-C₁₀H₇)₂Ca·2 OC₄H₈
Formation: 5.4.3.2.2
- C₂₈H₄₄GaK**
K[(n-C₅H₁₁C≡C)₄Ga]
Formation: 5.3.4.4.1
- C₂₈H₆₀GaNa**
Na[(n-C₇H₁₅)₄Ga]
Formation: 5.3.4.4.1
- C₂₈H₇₈AlLiO₄Si₄**
Li[Al[Si(CH₃)₃]₄]·4 $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$
Formation: 5.3.8.4
- C₂₉H₂₀AlN**
(C₆H₅C≡C)₃Al·NC₅H₅
Formation: 5.3.3.2.3
- C₃₀H₂₁B**
(1-naphthyl)₃B
Reaction with BeR₂: 5.4.3.4.4
- C₃₀H₂₇Fe₃Tl**
(h⁵-C₅H₅FeC₅H₄·h⁵)₃Tl
Formation: 5.3.6.3.2
- C₃₀H₃₉Ga**
[4-(CH₃)₃CC₆H₄]₃Ga
Formation: 5.3.4.2.3
- C₃₀H₃₉In**
[4-(CH₃)₃CC₆H₄]₃In
Formation: 5.3.5.2.5
- C₃₀H₅₁B**
{6,6-(CH₃)₂-bicyclo[3.1.1]C₇H₉}₃B
Formation: 5.3.2.5.1
- C₃₀H₅₄Be₂N₂**
[(Me₃CC≡C)₂Be·N(CH₃)₃]₂
Redistribution with BeR₂: 5.4.3.4.4
- C₃₀H₆₃Al**
(n-C₁₀H₂₁)₃Al
Formation: 5.3.3.2.2
- C₃₀H₆₃Ga**
(n-C₁₀H₂₁)₃Ga
Formation: 5.3.4.4.1, 5.3.4.4.2, 5.3.4.5.2
- C₃₀H₆₃In**
(n-C₁₀H₂₁)₃In
Formation: 5.3.5.4.1
- C₃₁H₂₅Al**
(C₆H₅)₂AlC(C₆H₅)₃
Formation: 5.3.3.5.5
Thermal decomposition: 5.3.3.5.5
- C₃₁H₂₅BeNa**
NaBe(C₆H₅)₂[C(C₆H₅)₃]
Formation: 5.4.3.4.4
- C₃₂H₂₀AlLi**
Li[(C₆H₅C≡C)₄Al]
Formation: 5.3.3.5.2
- C₃₂H₂₀BaHg**
BaHg(C≡CC₆H₅)₄
Formation: 5.4.3.3.1
- C₃₂H₂₀BeLi₂**
Li₂Be(C≡CC₆H₅)₄
Formation: 5.4.3.4.4
- C₃₂H₂₀F₂₀NTl**
[(C₂H₅)₄N][Ti(C₆F₅)₄]
Formation: 5.3.6.3.1
- C₃₂H₂₅Al**
(C₆H₅)₂C=C(C₆H₅)Al(C₆H₅)₂
Formation: 5.3.3.5.2
Thermal decomposition, cyclization: 5.3.3.5.2
- C₃₂H₅₂AlLi**
Li[(C₆H₉CH₂CH₂)₄Al]
Formation: 5.3.3.4.1
- C₃₂H₅₂GaK**
K[(n-C₆H₁₃C≡C)₄Ga]
Formation: 5.3.4.4.1

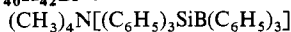
- C₃₂H₆₈GaNa**
Na[(n-C₈H₁₇)₄Ga]
Formation: 5.3.4.4.1
- C₃₃H₆₉Al**
(n-C₁₁H₂₃)₃Al
Formation: 5.3.3.2.2
- C₃₄H₃₀Ge₂**
[1-C₁₀H₇(C₆H₅)CH₃Ge]₂
Formation: 5.4.5.3
- C₃₄H₃₄CaO₂**
(Fluorenyl)₂Ca·2 OC₄H₈
Formation: 5.4.3.4.2
- C₃₆H₁₅F₁₅InP**
(C₆F₅)₃In·P(C₆H₅)₃
Formation: 5.3.5.2.6
- C₃₆H₃₀BGeLi**
Li[(C₆H₅)₃GeB(C₆H₅)₃]
Cation exchange reactions: 5.3.12.2.2
- C₃₆H₃₀BLiSi**
Li[(C₆H₅)₃SiB(C₆H₅)₃]
Cation exchange: 5.3.7.4.2
Formation: 5.3.7.4.2
- C₃₆H₃₀BaGe₂**
Ba[(C₆H₅)₃Ge]₂
Formation: 5.4.5.6
- C₃₆H₃₀BaSi₂**
Ba[(C₆H₅)₃Si]₂
Formation: 5.4.4.6
- C₃₆H₃₀Br₂Mg₂Sn₂**
[(C₆H₅)₂Sn·C₆H₅MgBr]₂
Formation: 5.4.6.5
- C₃₆H₃₀CaSi₂**
Ca[(C₆H₅)₃Si]₂
Formation: 5.4.4.6
- C₃₆H₃₀Cl₂NiP₂**
[(C₆H₅)₃P]₂NiCl₂
Catalyst for RMgX reactions: 5.4.2.5.1
Catalyst for isomerization of cis- or trans-RMgX: 5.4.2.5.3
Catalyst in the reaction of α-NpPhMe*
GeH with RMgX: 5.4.5.3
- C₃₆H₃₀Ge₂**
(C₆H₅)₃GeGe(C₆H₅)₃
Reaction with Sr and Ba metals: 5.4.5.6
- C₃₆H₃₀Ge₂Mg**
Mg[(C₆H₅)₃Ge]₂
Formation: 5.4.5.2
- C₃₆H₃₀Ge₂Sr**
Sr[(C₆H₅)₃Ge]₂
Formation: 5.4.5.6
- C₃₆H₃₀MgSn₂**
Mg[(C₆H₅)₃Sn]₂
Formation: 5.4.6.2, 5.4.6.3
- C₃₆H₃₀Pb₂**
(C₆H₅)₃PbPb(C₆H₅)₃
Reaction with RMgX: 5.4.7.2.2
Reaction with group-IIA metals:
5.4.7.2.1
- C₃₆H₃₀Si₂**
(C₆H₅)₃SiSi(C₆H₅)₃
Formation: 5.4.4.2
Reaction with LiAlH₄: 5.3.8.7
Reaction with Ca, Sr and Ba metals:
5.4.4.6
- C₃₆H₃₀Si₂Sr**
Sr[(C₆H₅)₃Si]₂
Formation: 5.4.4.6
- C₃₆H₃₀Sn₂**
(C₆H₅)₃SnSn(C₆H₅)₃
Formation: 5.3.17.2.2
Reaction with Mg metal: 5.4.6.3
- C₃₆H₆₉B**
(cyclo-C₁₂H₂₃)₃B
Thermal decomposition: 5.3.2.6.3
- C₃₆H₇₅Al**
(n-C₁₂H₂₅)₃Al
Formation: 5.3.3.2.2
- C₃₆H₉₉Ge₃Si₉Tl**
{[(CH₃)₃SiCH₂]₃Ge}₃Tl
Formation: 5.3.16
- C₃₆H₉₉Si₉Sn₃Tl**
{[(CH₃)₃SiCH₂]₃Sn}₃Tl
Formation: 5.3.21.1
- C₃₇H₃₀ClIrOP₂**
Ir(CO)Cl[P(C₆H₅)₃]₂
Hydroboration catalyst: 5.3.2.7.1
- C₃₈H₅F₃₀Ge₂Tl**
[(C₆F₅)₃Ge]₂TlC₂H₅
Formation: 5.3.16
- C₃₈H₃₀Ba**
Ba[C(C₆H₅)₃]₂
Polymerization of dienes: 5.4.3.4.1
Polymerization of styrene: 5.4.3.4.1
- C₃₈H₃₀Mg**
Mg[C(C₆H₅)₃]₂
Formation: 5.4.2.2.3, 5.4.2.3.1, 5.4.2.3.3
- C₃₈H₃₅AlO**
(C₆H₅)₅C₄Al·O(C₂H₅)₂
Formation: 5.3.3.3.1
- C₃₈H₃₅AlSi₂**
[(C₆H₅)₃Si]₂AlC₂H₅
Formation: 5.3.8.2.1
- C₃₉H₆₃In**
(n-C₈H₁₇C₅H₄)₃In
Formation: 5.3.5.2.5

C₄₀H₃₈BaGe₂O

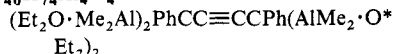
Formation: 5.4.5.6

C₄₀H₃₈Ge₂OSr

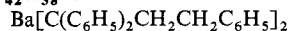
Formation: 5.4.5.6

C₄₀H₄₂BNSi

Formation: 5.3.7.4.2

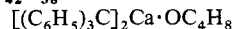
C₄₀H₇₄Al₄O₄

Formation: 5.3.3.3.4

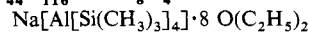
C₄₂H₃₈Ba

Formation: 5.4.3.4.1

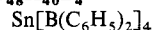
Polymerization of styrene: 5.4.3.4.1

C₄₂H₃₈CaO

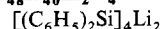
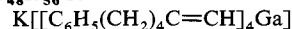
Formation: 5.4.3.4.2

C₄₄H₁₁₆AlNaO₈Si₄

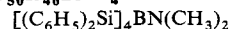
Formation: 5.3.8.5

C₄₈H₄₀B₄Sn

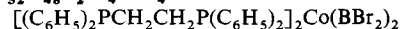
Formation: 5.3.17.3.1

C₄₈H₄₀Li₂Si₄Reaction with (R₂N)₂BX: 5.3.7.4.1**C₄₈H₅₆GaK**

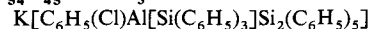
Formation: 5.3.4.4.1

C₅₀H₄₆BNSi₄

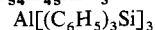
Formation: 5.3.7.4.1

C₅₂H₄₈B₂Br₄CoP₄

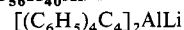
Reaction with tin halides: 5.3.17.3.1

C₅₄H₄₅AlClKSi₃

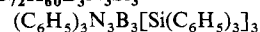
Formation: 5.3.8.2.1

C₅₄H₄₈AlSi₃

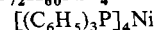
Formation: 5.3.8.2.1

C₅₆H₄₀AlLi

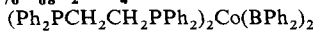
Formation: 5.3.3.3.1

C₇₂H₆₀B₃N₃Si₃

Formation: 5.3.7.4.1

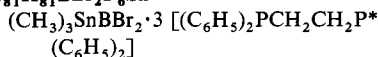
C₇₂H₆₀NiP₄

Catalyst for isomerization of cis- or trans-RMgX: 5.4.2.5.3

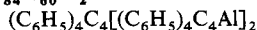
C₇₆H₆₈B₂CoP₄

Reaction with lead halides: 5.3.22.3.1

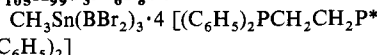
Reaction with tin halides: 5.3.17.3.1

C₈₁H₈₁BBr₂P₆Sn

Formation: 5.3.17.3.1

C₈₄H₆₀Al₂

Formation: 5.3.3.3.1

C₁₀₅H₉₉B₃Br₆P₈Sn

Formation: 5.3.17.3.1

Ca**Ca**Reaction with PbR₄: 5.4.7.2.3

Reaction with Pb metal: 5.4.7.1.1

Reaction with R₂Hg, R₂Zn: 5.4.3.2.2Reaction with R₆Si₂: 5.4.4.6

Reaction with Sn metal: 5.4.6.1

Reaction with RX: 5.4.3.2.1

Reaction with C₅H₆: 5.4.3.2.3**Ca*₂****Ca*₂****Ca*₂H₆****Ca*₈H₁₈****Ca*₈H₂₀Al****Ca*₈H₂₀B****Ca*₁₀H₁₀****Ca*₁₀H₁₀****Ca*₁₂H₁₀****Ca*₁₄H₁₄****Ca*₁₆H₁₀****Ca*₁₆H₄₀Al₂****Ca*₁₆H₄₀Al₂****Ca*₁₇H₂₇Al****Ca*₁₈H₁₄****Ca*₂₆H₂₂****CaCl*₁₉H₁₅****CaClO₂*₂₁H₂₅****CaClO₂*₂₇H₃₁****CaF₅I*₆****CaH₂****CaH₂**Reaction with C₅H₆: 5.4.3.4.2

Reaction with olefins: 5.4.3.4.3

CaH₄N₂

Metallation by: 5.4.3.4.2

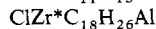
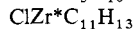
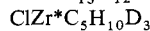
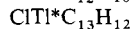
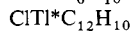
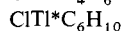
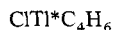
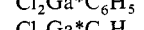
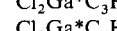
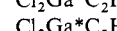
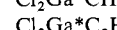
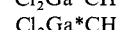
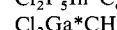
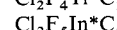
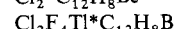
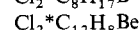
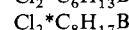
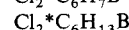
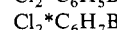
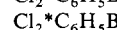
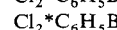
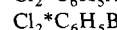
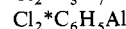
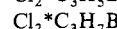
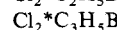
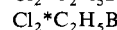
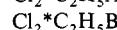
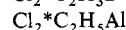
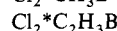
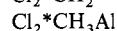
CaI*₃CH₃

- CaI*CH₃
 CaI*CH₃
 CaI*C₂H₅
 CaI*C₃H₇
 CaI*C₄H₉
 CaI*C₆H₅
 CaI*C₇H₁₅
 CaI*C₈H₅
 CaI*C₉H₇
 CaI*C₁₀H₇
 CaI*C₁₃H₉
 CaI*C₁₅H₁₅
 CaI*C₁₉H₁₅
 CaIN₂*C₁₂H₁₇
 CaIO*C₇H₇
 CaIO₂*C₁₀H₁₃
 CaIO₂*C₁₁H₁₅
 CaIO₂*C₁₃H₂₁
 CaN*C₁₆H₁₆
 CaO*C₄₂H₃₈
 CaO₂*C₄H₁₀
 CaO₂*C₁₈H₂₆
 CaO₂*C₂₀H₂₆
 CaO₂*C₂₂H₃₀
 CaO₂*C₂₆H₃₀
 CaO₂*C₂₈H₃₀
 CaO₂*C₃₄H₃₄
CaPb
 CaPb
 Formation: 5.4.7.1.1
CaPb₃
 CaPb₃
 Formation: 5.4.7.1.1, 5.4.7.1.2
 CaSi₂*C₃₆H₃₀
CaSn
 CaSn
 Formation: 5.4.6.1
CaSn₃
 CaSn₃
 Formation: 5.4.6.1
 CaZn*C₈H₂₀
Ca₂Pb
 Ca₂Pb
 Formation: 5.4.7.1.1
Ca₂Sn
 Ca₂Sn
 Formation: 5.4.6.1
Ca₅Pb₃
 Ca₅Pb₃
 Formation: 5.4.7.1.1
 Cd*C₂H₆
 Cd*C₄H₁₀
 Cd*C₁₂H₁₀
 Cl*CH₃
 Cl*C₂H₅
 Cl*C₂H₅Be
 Cl*C₂H₆Al
 Cl*C₂H₆Al
 Cl*C₂H₆B
 Cl*C₄H₆B
 Cl*C₄H₈B
 Cl*C₄H₉Be
 Cl*C₄H₁₀Al
 Cl*C₄H₁₀Al
 Cl*C₄H₁₀Al
 Cl*C₄H₁₀Al
 Cl*C₄H₁₀Al
 Cl*C₄H₁₀B
 Cl*C₄H₁₀B
 Cl*C₄H₁₀B
 Cl*C₅H₅Be
 Cl*C₅H₁₀B
 Cl*C₆H₁₂B
 Cl*C₆H₁₄B
 Cl*C₈H₁₈Al
 Cl*C₈H₁₈Al
 Cl*C₈H₁₈B
 Cl*C₉H₉B
 Cl*C₁₀H₁₈B
 Cl*C₁₂H₁₀B
 Cl*C₁₂H₂₆B
 Cl*C₁₉H₁₅Ba
 Cl*C₁₉H₁₅Ca
 ClF₂Sn*C₄H₁₀Al
 ClF₄*C₁₂H₁₀B
 ClF₄N₂*C₆H₄B
 ClF₆*C₄B
 ClF₁₀In*C₁₂
 ClGa*C₂H₆
 ClGa*C₄H₁₀
 ClGa*C₈H₁₈
 ClGa*C₁₂H₁₀
 ClGaN*C₃H₁₁
 ClGaSi₂*C₈H₂₂
ClGeH₃
 H₃GeCl
 Reaction with Na[C₂B₄H₇]: 5.3.12.3
 ClGe*C₃H₉
 ClGe*C₁₈H₁₅
 ClGe*H₃
 ClGeMg*C₁₇H₁₅
 ClGeMg*C₁₈H₁₅
ClHMg
 HMgCl
 Addition to alkynes: 5.4.2.4.1

- Addition to olefins: 5.4.2.4.1
- ClH₃Si**
 H₃SiCl
 Reaction with LiB₅H₈: 5.3.7.3.2
- ClIn**
 InCl
 Reaction with RHgX: 5.3.5.3.4
 Reaction with R₂Hg: 5.3.5.3.4
- ClIn***C₂H₆
ClIn*C₄H₁₀
ClIn*C₁₂H₁₀
ClInSi₂*C₈H₂₂
ClIrOP₂*C₃₇H₃₀
- ClK**
 KCl
 Complex formation with R₂AlCl,
 RAlCl₂, AlCl₃: 5.3.3.3.2
 Complexing agent for aluminumalkyls:
 5.3.5.3.1
- ClKSi***C₈H₂₁Al
ClKSi₃*C₅₄H₄₅Al
ClMg*CH₃
ClMg*C₂H₅
ClMg*C₃H₅
ClMg*C₃H₇
ClMg*C₄H₇
ClMg*C₄H₉
ClMg*C₄H₉
ClMg*C₄H₉
ClMg*C₄H₉
ClMg*C₅H₉
ClMg*C₅H₁₁
ClMg*C₅H₁₁
ClMg*C₆H₅
ClMg*C₆H₁₁
ClMg*C₇H₇
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ClMg*C₉H₇
ClMg*C₉H₁₁
ClMg*C₁₀H₁₈
ClMg*C₁₁H₉
ClMg*C₁₁H₉
ClMg*C₁₁H₁₅
ClMgO*C₂H₅
ClMgOSi*C₇H₁₇
ClMgO₂*C₇H₁₃
ClMgPb*C₃H₉
ClMgPb*C₆H₁₅
ClMgPb*C₁₅H₃₃
- ClMgPb***C₁₈H₁₅
ClMgPbSi₃*C₁₂H₃₃
ClMgSi*C₄H₁₁
ClMgSn*C₁₂H₂₇
ClN*C₄H₁₀B
ClN*C₆H₁₃B
ClN*C₁₁H₂₂Be
ClNSn*C₇H₁₉B
ClN₂*C₂H₄B
ClN₂*C₃H₆B
ClN₂*C₄H₁₀B
ClN₂*C₄H₁₂B
ClN₂*C₄H₁₂B
ClN₂*C₄H₁₂B
ClN₂*C₈H₂₀B
ClN₂*C₁₂H₁₁Be
ClNa
 NaCl
 Complex formation with RAlCl₂:
 5.3.3.3.2
- ClO***C₄H₁₀B
ClO*C₄H₁₂Al
ClO*C₄H₁₂B
ClO*C₄H₁₂B
ClO*C₇H₅
ClOSi*C₇H₁₇
ClOSi₄*C₁₈H₄₈Al
ClO₂*C₂H₄B
ClO₂*C₂H₆B
ClO₂*C₂H₆B
ClO₂*C₅H₁₁Be
ClO₂*C₈H₁₉Be
ClO₂*C₁₀H₁₃Be
ClO₂*C₂₁H₂₅Ca
ClO₂*C₂₇H₃₁Ca
ClPb*C₃H₉
ClS*C₂H₈B
ClS*C₇H₁₄BBr₂
ClS*C₈H₂₀B
ClSi*C₃H₉
ClSi*C₃H₉
ClSi*C₃H₉
ClSi*C₃H₁₆B₅
ClSi*C₄H₁₁
ClSi*C₄H₁₁
ClSi*C₅H₁₅B₄
ClSi*C₆H₁₅
ClSi*C₁₈H₁₅
ClSi₂Tl*C₆H₁₈
ClSi₄*C₁₄H₃₈Al
ClSn*C₃H₉
ClSn*C₁₈H₁₅
- ClTi**
 TiCl
 Reaction with RLi and RI: 5.3.6.3.2

CITl, *contd*Reaction with elemental X_2 : 5.3.6.3.1

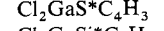
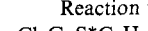
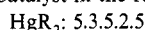
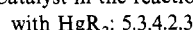
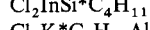
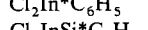
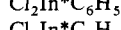
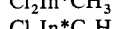
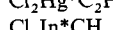
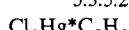
Reaction with potassium metal: 5.3.6.2.1

**Cl₂**Reaction with B_2O_3 and elemental carbon: 5.3.2.2.2Reaction with TiCl_4 : 5.3.6.3.1**Cl₂GaH**

Formation: 5.3.4.4.1

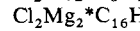
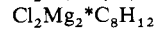
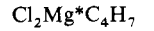
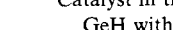
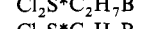
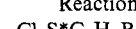
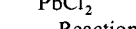
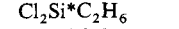
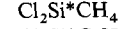
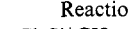
Reaction with alkynes: 5.3.4.4.1

Reaction with olefins: 5.3.4.4.1

**Cl₂H₂Si**Reaction with $\text{LiC}_2\text{B}_4\text{H}_7$: 5.3.7.3.2**Cl₂Hg**Catalyst in RMgX formation: 5.4.2.2.1Catalyst in the reaction of In withCatalyst in the reaction of Ga metalReaction with In metal and HgPh_2 :**Cl₂Mg**

Formation: 5.4.6.2

Preparation of active form: 5.4.2.3.1

Reaction with RLi : 5.4.2.3.1Reaction with RNA : 5.4.2.3.1Redistribution with MgR_2 : 5.4.2.3.2Removal after RMgX reaction: 5.4.3.3.1**Cl₂Ni**Catalyst for RMgX —olefin exchange:
5.4.2.5.3Catalyst for isomerization of *cis*- or
trans- RMgX : 5.4.2.5.3Catalyst in the reaction of $\alpha\text{-NpPhMe}^*$
 GeH with RMgX : 5.4.5.3**Cl₂Pb**Reaction with RMgX : 5.4.7.2.5**Cl₂Si**Reaction with BX_3 : 5.3.7.2**Cl₂Sn**Reaction with $\text{Na}[\text{C}_2\text{B}_4\text{H}_7]$: 5.3.17.3.2

- Reaction with $\text{Na}[\text{C}_2\text{B}_9\text{H}_{11}]$: 5.3.17.3.2
 Reaction with $\text{Na}[\text{Me}_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}$:
 5.3.17.3.2
- $\text{Cl}_2\text{Sn}^*\text{C}_2\text{H}_6$
 $\text{Cl}_2\text{Ti}^*\text{C}_4\text{H}_{10}$
 $\text{Cl}_2\text{Ti}^*\text{C}_{10}\text{H}_{10}$
 $\text{Cl}_2\text{Ti}^*\text{C}_{10}\text{H}_{10}$
 $\text{Cl}_2\text{Ti}^*\text{C}_{10}\text{H}_{10}$
 $\text{Cl}_2\text{Ti}^*\text{C}_2\text{H}_3$
 $\text{Cl}_2\text{Ti}^*\text{C}_3\text{H}_5$
 $\text{Cl}_2\text{Ti}^*\text{C}_7\text{H}_7$
 $\text{Cl}_2\text{Ti}^*\text{C}_8\text{H}_9$
 $\text{Cl}_2\text{Zr}^*\text{C}_{10}\text{H}_{10}$
 Cl_3^*Al
 Cl_3^*Al
 Cl_3^*Al
 Cl_3^*Al
 Cl_3^*B
 Cl_3^*B
 Cl_3^*B
 Cl_3^*B
 Cl_3^*B
 Cl_3^*B
 Cl_3^*B
 Cl_3^*CH
 $\text{Cl}_3^*\text{C}_2\text{H}_2\text{B}$
 $\text{Cl}_3^*\text{C}_3\text{H}_9\text{Al}_2$
 $\text{Cl}_3^*\text{C}_3\text{H}_9\text{Al}_2$
 $\text{Cl}_3^*\text{C}_6\text{H}_{15}\text{Al}_2$
 $\text{Cl}_3^*\text{C}_6\text{H}_{15}\text{Al}_2$
 $\text{Cl}_3^*\text{C}_8\text{H}_6\text{B}$
 $\text{Cl}_3^*\text{C}_{18}\text{H}_{12}\text{B}$
 $\text{Cl}_3^*\text{C}_{18}\text{H}_{15}\text{Al}_2$
 Cl_3Fe
 FeCl_3
 Catalyst for RMgX —olefin exchange:
 5.4.2.5.3
- Cl_3Ga
 GaCl_3
 Reaction with GeR_4 : 5.3.4.3.1
 Reaction with RLi : 5.3.4.3.1
 Reaction with R_2Zn : 5.3.4.3.1
 Reaction with R_3Ga : 5.3.4.3.5
 Reaction with R_3SiH : 5.3.4.4.1
 Reaction with SiR_4 : 5.3.4.3.1
 Reaction with SnR_4 : 5.3.4.3.1
 Reaction with carbon—silicon bonds:
 5.3.4.3.2
 Reaction with Li metal and R_3SiCl :
 5.3.9
- $\text{Cl}_3\text{Ga}^*\text{C}_{18}\text{H}_{12}$
- $\text{Cl}_3\text{GaSn}^*\text{C}_4\text{H}_{12}$
 $\text{Cl}_3\text{Ge}^*\text{CH}_3$
 $\text{Cl}_3\text{In}_2^*\text{CH}_2$
 Cl_3In
 InCl_3
 Reaction with InR_3 : 5.3.5.3.2
 Reaction with Li metal and R_3SiX :
 5.3.10
 Reaction with potassium metal: 5.3.5.2.2
- $\text{Cl}_3\text{In}^*\text{C}_{18}\text{H}_{12}$
 $\text{Cl}_3\text{In}_2^*\text{CH}_2\text{Br}$
 $\text{Cl}_3\text{Mg}_2^*\text{C}_2\text{H}_5$
 $\text{Cl}_3\text{N}_3^*\text{C}_3\text{H}_9\text{B}_3$
 $\text{Cl}_3\text{N}_3^*\text{C}_{18}\text{H}_{15}\text{B}_3$
 $\text{Cl}_3\text{Na}^*\text{CH}_3\text{Al}$
 $\text{Cl}_3\text{O}_{12}\text{Ti}$
 $\text{Ti}(\text{ClO}_4)_3$
 Thallating agent: 5.3.6.3.4
- $\text{Cl}_3\text{Si}^*\text{CH}_{10}\text{B}_5$
 $\text{Cl}_3\text{Sn}^*\text{C}_{24}\text{H}_{20}\text{As}$
 Cl_3Ti
 TiCl_3
 Polymerization catalyst: 5.3.3.5.1
- $\text{Cl}_3\text{Ti}^*\text{C}_5\text{H}_5$
 Cl_3Ti
 TiCl_3
 Formation: 5.3.6.3.1
 Reaction with $\text{RB}(\text{OH})_2$: 5.3.6.3.3
 Thallating agent: 5.3.6.3.4
- $\text{Cl}_3\text{Ti}^*\text{C}_2\text{H}_4$
 Cl_4^*B_2
 Cl_4^*C
 $\text{Cl}_4^*\text{CH}_2\text{Al}_2$
 $\text{Cl}_4^*\text{C}_2\text{H}_2\text{B}_2$
 $\text{Cl}_4^*\text{C}_3\text{H}_6\text{B}_2$
 $\text{Cl}_4^*\text{C}_6\text{H}_{10}\text{B}_2$
 $\text{Cl}_4\text{Ga}_2^*\text{C}_2\text{H}_4$
 Cl_4Ge
 GeCl_4
 Reaction with RAl : 5.3.13.5
 Reaction with RMgX : 5.4.5.2
- $\text{Cl}_4\text{In}_2^*\text{CH}_2$
 $\text{Cl}_4\text{Mg}^*\text{C}$
 $\text{Cl}_4\text{O}_4\text{Si}_4^*\text{C}_4\text{H}_{12}$
 Cl_4Si
 SiCl_4
 Reaction with elemental Si: 5.3.7.2
- $\text{Cl}_4\text{Si}^*\text{CH}_2$
 Cl_4Sn
 SnCl_4
 Exchange with R_3Al : 5.3.3.5.4
- Cl_4Ti
 TiCl_4
 Carbometallation with Me_3Al : 5.3.3.5.1

Cl₄Ti, *contd*

Catalyst for RMgX—olefin exchange:

5.4.2.5.3

Catalyst for hydroalumination: 5.3.3.4.1

Catalyst for reaction of RMgX with
olefins: 5.4.2.5.3

Polymerization catalyst: 5.3.3.5.1

Cl₄ZrZrCl₄

Catalyst for RMgX—olefin exchange:

5.4.2.5.3

Cl₅Si*B**Cl₅Tl***C₅**Cl₆***C₂B₂**Cl₆Ga***C₁₂H₃₀Al₃**Cl₇Cs₂N₃***C₃B₁₀**Cl₈***CB₄**Cl₈***C₂H₂B₄**Cl₈***C₁₀H₈B₄**Cl₉O₆Tl***C₃**Cl₁₀Cs₂***B₁₀**Co***C₁₀H₁₀**Co***C₁₆H₁₅B**CoGeO₄***C₂₂H₁₅**CoLi***C₈H₅B₂**CoO₄Si***C₂₁H₁₅**CoO₄Si***C₂₂H₁₅**CoP₄***C₅₂H₄₈B₂Br₄**CoP₄***C₇₆H₆₈B₂**Co₂O₆***C₁₀H₆**Co₂Sn***C₁₆H₁₀B₄**CrO₃***C₉H₆**Cs₂***B₁₀Cl₁₀**Cs₂N₃***C₃B₁₀Cl₇**CuI**

CuI

Reaction with alkynes: 5.4.2.4.1

CuO*C₄H₉**D***C₈H₁₈Al**DGaN***C₅H₁₅**DGe***C₁₈H₁₅**D₂GaN***C₄H₁₂**D₂O**D₂OReaction with Mg(GeR₃)₂: 5.4.5.2**D₃ClZr***C₅H₁₀**D₃IMg***C**D₄Tl***C₅H**D₅Tl***C₅**D₆Be***C₂**F***B**FHO₃S**FSO₃H

Thallation solvent: 5.3.6.3.4

FlIn*C₆H₄Br₂**FK**

KF

Reaction with R₃Al: 5.3.3.3.1**FK***C₈H₂₀Be₂**FMg***C₆H₁₃**FNa**

NaF

Reaction with R₂AlCl: 5.3.3.3.2**F₂***CH₃B**F₂***C₂HB**F₂***C₂H₃B**F₂***C₂H₅B**F₂***C₈H₁₂B₂**F₂In***C₁₂H₈Br**F₂Mg**MgF₂Reaction with MgR₂: 5.4.2.3.2**F₂Na***C₂H₆Al**F₂Si**SiF₂

Formation: 5.3.7.2

Reaction with BX₃: 5.3.7.2**F₂Sn**SnF₂Reaction with R₂AlX: 5.3.18.4**F₂Sn***C₄H₁₀AlCl**F₃***Al**F₃***B**F₃***B**F₃***B**F₃***B**F₃***B**F₃***CH₃B**F₃***C₇H₅**F₃Ga***C₁₈H₁₂**F₃In***C₁₈H₁₂**F₃O***C₄H₁₀B**F₃Sb**SbF₃

Halogen exchange: 5.3.2.3.1

F₄*B₂**F₄***C₂H₂B₂**F₄***C₁₂H₁₀BBr**F₄***C₁₂H₁₀BCl**F₄I***C₁₂H₁₀B**F₄K***B**F₄K***B**F₄N₂***C₆H₄BCl**F₄N₂***C₆H₅B**F₄N₂***C₇H₇B**F₄N₂***C₈H₉B

$F_4N_2O \cdot C_7H_7B$
 $F_4N_2O \cdot C_8H_9B$
 $F_4O \cdot C_6H_{15}B$
 $F_4O_2Ti \cdot C_{14}H_{14}B$
 $F_4O_2Ti \cdot C_{16}H_{18}B$
 F_4Si

SiF₄

Reaction with elemental B: 5.3.7.2

Reaction with elemental Si: 5.3.7.2

$F_4Ti \cdot C_{12}H_8BCl_2$
 $F_4Ti \cdot C_{12}H_{10}B$
 $F_4Ti \cdot C_{14}H_{14}B$
 $F_4Ti \cdot C_{16}H_{18}B$
 $F_5 \cdot C_6H$
 $F_5 \cdot C_{11}H_5Be$
 $F_5I \cdot C_6$
 $F_5I \cdot C_6Ca$
 $F_5I_2In \cdot C_6$
 $F_5In \cdot C_6Cl_2$
 $F_5Li \cdot C_6$
 $F_5Mg \cdot C_6Br$
 F_5Sb

SbF₅

Addition to thallating agents: 5.3.6.3.4

$F_6 \cdot C_4BCl$

F_6K_2Si

$K_2[SiF_6]$

Reaction with $K[BF_4]$: 5.3.7.1

$F_6Na_3 \cdot Al$
 $F_6O_4Ti \cdot C_{11}H_7$
 $F_6O_5Ti \cdot C_{11}H_{15}$
 $F_6Si \cdot B_2$
 $F_6Sn \cdot C_6H_6$
 $F_7Si \cdot B_3$
 $F_7Si_2 \cdot B$
 $F_8 \cdot C_3B_4$
 $F_9 \cdot C_6Al$
 $F_9O_6S_2Ti \cdot C_8H_2$
 $F_9O_6Ti \cdot C_6$
 $F_9O_6Ti \cdot C_6$
 $F_9O_6S_3Ti \cdot C_3$
 $F_9Si_3 \cdot B$
 $F_{10}Ge \cdot C_{12}H_2$
 $F_{10}In \cdot C_{12}$
 $F_{10}In \cdot C_{12}Br$
 $F_{10}In \cdot C_{12}Cl$
 $F_{10}O_6S_2Ti \cdot C_8H$
 $F_{10}O_6S_2Ti \cdot C_9H_3$
 $F_{10}O_7S_2Ti \cdot C_9H_3$
 $F_{10}Ti \cdot C_{12}Br$
 $F_{11}O_6S_2Ti \cdot C_8$
 $F_{11}Si_4 \cdot B$

$F_{12}O_3Ti \cdot C_{21}H_9$
 $F_{12}Ti \cdot C_{18}H_3$
 $F_{13}Si_5 \cdot B$
 $F_{15}GaO \cdot C_{22}H_{10}$
 $F_{15}Ge \cdot C_{18}H$
 $F_{15}In \cdot C_{18}$
 $F_{15}In \cdot C_{18}$
 $F_{15}In \cdot C_{18}$
 $F_{15}InO \cdot C_{22}H_{10}$
 $F_{15}InP \cdot C_{36}H_{15}$
 $F_{15}MgPb \cdot C_{18}Br$
 $F_{15}Ti \cdot C_{18}$
 $F_{20}NTi \cdot C_{32}H_{20}$
 $F_{30}Ge_2Ti \cdot C_{38}H_5$
 $Fe \cdot C_{10}H_8B_2Br_4$
 $Fe \cdot C_{10}H_9BBr_2$
 $Fe \cdot C_{10}H_{10}$
 $Fe \cdot Cl_3$
 $FeI \cdot C_{10}H_9$
 $FeI \cdot C_{11}H_{12}B$
 $FeI \cdot C_{16}H_{14}B$
 $FeI_2 \cdot C_{10}H_9B$
 $FeI_4 \cdot C_{10}H_8B_2$
 $FeMg_2 \cdot C_{10}H_8Br_2$
 $FeNa \cdot C_8H_{21}B_8$
 $FeNa_2 \cdot C_{10}H_8$
 $FeO_3 \cdot C_3H_8B_4$
 $FeSn \cdot C_8H_{12}B_8$
 $Fe_3Ti \cdot C_{30}H_{27}$
Ga

Ga

Reaction with $Hg(SiR_3)_2$: 5.3.9

Reaction with RX: 5.3.4.2.1

Reaction with I₂: 5.3.4.2.1

Reaction with Li and R₃SiX: 5.3.9

Use as an anode: 5.3.4.2.4

$Ga \cdot Br_2$

$Ga \cdot Br_3$

$Ga \cdot Br_3$

$Ga \cdot Br_3$

$Ga \cdot CH_3Cl_2$

$Ga \cdot CH_3Cl_2$

$Ga \cdot C_2H_3Cl_2$

$Ga \cdot C_2H_5Cl_2$

$Ga \cdot C_2H_6Cl$

$Ga \cdot C_3H_7Cl_2$

$Ga \cdot C_3H_9$

$Ga \cdot C_3H_9$

$Ga \cdot C_3H_9$

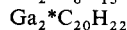
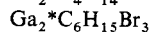
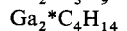
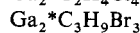
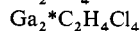
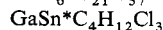
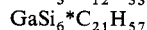
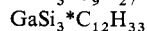
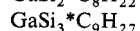
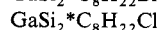
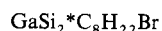
$Ga \cdot C_3H_9$

$Ga \cdot C_4H_{10}Cl$

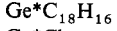
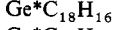
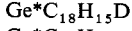
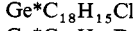
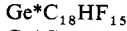
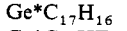
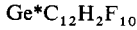
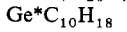
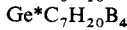
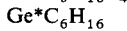
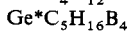
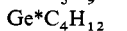
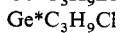
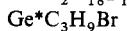
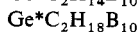
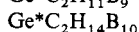
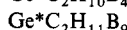
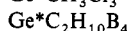
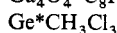
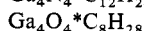
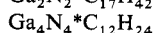
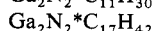
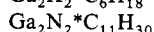
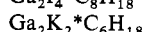
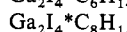
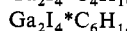
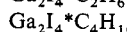
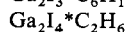
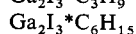
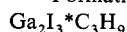
$Ga \cdot C_4H_{11}$

$\text{Ga}^*\text{C}_6\text{H}_5\text{Br}_2$
 $\text{Ga}^*\text{C}_6\text{H}_5\text{Cl}_2$
 $\text{Ga}^*\text{C}_6\text{H}_9$
 $\text{Ga}^*\text{C}_6\text{H}_{15}$
 $\text{Ga}^*\text{C}_7\text{H}_{11}$
 $\text{Ga}^*\text{C}_7\text{H}_{15}\text{Cl}_2$
 $\text{Ga}^*\text{C}_8\text{H}_{18}\text{Br}$
 $\text{Ga}^*\text{C}_8\text{H}_{18}\text{Cl}$
 $\text{Ga}^*\text{C}_8\text{H}_{19}$
 $\text{Ga}^*\text{C}_8\text{H}_{24}\text{As}$
 $\text{Ga}^*\text{C}_9\text{H}_{15}$
 $\text{Ga}^*\text{C}_9\text{H}_{21}$
 $\text{Ga}^*\text{C}_{10}\text{H}_{19}$
 $\text{Ga}^*\text{C}_{10}\text{H}_{21}$
 $\text{Ga}^*\text{C}_{12}\text{H}_{10}\text{Br}$
 $\text{Ga}^*\text{C}_{12}\text{H}_{10}\text{Cl}$
 $\text{Ga}^*\text{C}_{12}\text{H}_{27}$
 $\text{Ga}^*\text{C}_{12}\text{H}_{30}\text{Al}_3\text{Cl}_6$
 $\text{Ga}^*\text{C}_{14}\text{H}_{31}$
 $\text{Ga}^*\text{C}_{14}\text{H}_{31}$
 $\text{Ga}^*\text{C}_{15}\text{H}_{33}$
 $\text{Ga}^*\text{C}_{18}\text{H}_{12}\text{Br}_3$
 $\text{Ga}^*\text{C}_{18}\text{H}_{12}\text{Cl}_3$
 $\text{Ga}^*\text{C}_{18}\text{H}_{12}\text{F}_3$
 $\text{Ga}^*\text{C}_{18}\text{H}_{15}$
 $\text{Ga}^*\text{C}_{18}\text{H}_{27}$
 $\text{Ga}^*\text{C}_{18}\text{H}_{33}$
 $\text{Ga}^*\text{C}_{21}\text{H}_{21}$
 $\text{Ga}^*\text{C}_{24}\text{H}_{27}$
 $\text{Ga}^*\text{C}_{27}\text{H}_{21}$
 $\text{Ga}^*\text{C}_{27}\text{H}_{33}$
 $\text{Ga}^*\text{C}_{30}\text{H}_{39}$
 $\text{Ga}^*\text{C}_{30}\text{H}_{63}$
 Ga^*Cl_3
 Ga^*Cl_3
 Ga^*Cl_3
 $\text{GaGe}_2^*\text{C}_{12}\text{H}_{30}\text{Br}$
 $\text{GaGe}_3^*\text{C}_{18}\text{H}_{45}$
 GaH^*Br_2
 GaH^*Cl_2
 GaH^*Cl_2
 GaH_3
 GaH_3
 Not known: 5.3.4.4.1
 GaH_4K
 $\text{K}[\text{GaH}_4]$
 Reaction with alkynes: 5.3.4.4.1
 GaH_4Na
 $\text{Na}[\text{GaH}_4]$
 Reaction with alkynes: 5.3.4.4.1
 Reaction with olefins: 5.3.4.4.1
 $\text{GaI}^*\text{C}_5\text{H}_{10}$

$\text{GaI}^*\text{C}_5\text{H}_{12}$
 $\text{GaI}^*\text{C}_{12}\text{H}_{10}$
 $\text{GaI}_2^*\text{C}_6\text{H}_5$
 GaI_3
 GaI_3
 Reaction with R_3Ga : 5.3.4.3.5
 $\text{GaK}^*\text{C}_4\text{H}_{12}$
 $\text{GaK}^*\text{C}_8\text{H}_{20}$
 $\text{GaK}^*\text{C}_{24}\text{H}_{36}$
 $\text{GaK}^*\text{C}_{28}\text{H}_{44}$
 $\text{GaK}^*\text{C}_{32}\text{H}_{52}$
 $\text{GaK}^*\text{C}_{48}\text{H}_{56}$
 $\text{GaKN}_2^*\text{C}_4\text{H}_6$
 $\text{GaLi}^*\text{C}_4\text{H}_{12}$
 $\text{GaLi}^*\text{C}_8\text{H}_{20}$
 $\text{GaLi}^*\text{C}_{12}\text{H}_{28}$
 $\text{GaLi}^*\text{C}_{16}\text{H}_{36}$
 $\text{GaLiO}_3\text{Si}_4^*\text{C}_{24}\text{H}_{66}$
 $\text{GaLiSn}^*\text{C}_6\text{H}_{18}$
 $\text{GaLi}_2^*\text{C}_{10}\text{H}_{25}$
 $\text{GaLi}_2^*\text{C}_{16}\text{H}_{40}\text{Al}$
 GaMg
 Ga-Mg
 Reaction with RX : 5.3.4.2.2
 $\text{GaN}^*\text{C}_3\text{H}_{11}\text{Cl}$
 $\text{GaN}^*\text{C}_3\text{H}_{12}$
 $\text{GaN}^*\text{C}_3\text{H}_{12}$
 $\text{GaN}^*\text{C}_4\text{H}_{12}\text{D}_2$
 $\text{GaN}^*\text{C}_4\text{H}_{14}$
 $\text{GaN}^*\text{C}_5\text{H}_{15}\text{D}$
 $\text{GaN}^*\text{C}_5\text{H}_{16}$
 $\text{GaN}^*\text{C}_6\text{H}_{18}$
 $\text{GaN}^*\text{C}_6\text{H}_{18}$
 $\text{GaN}_2^*\text{C}_8\text{H}_{21}$
 $\text{GaN}_2^*\text{C}_{11}\text{H}_{27}$
 $\text{GaNa}^*\text{C}_{24}\text{H}_{52}$
 $\text{GaNa}^*\text{C}_{28}\text{H}_{60}$
 $\text{GaNa}^*\text{C}_{32}\text{H}_{68}$
 GaO^*CH_3
 $\text{GaO}^*\text{C}_7\text{H}_7$
 $\text{GaO}^*\text{C}_7\text{H}_{19}$
 $\text{GaO}^*\text{C}_{10}\text{H}_{25}$
 $\text{GaO}^*\text{C}_{21}\text{H}_{21}$
 $\text{GaO}^*\text{C}_{22}\text{H}_{10}\text{F}_{15}$
 $\text{GaOSi}_3^*\text{C}_{13}\text{H}_{35}$
 $\text{GaO}_3^*\text{C}_{21}\text{H}_{21}$
 $\text{GaPSi}^*\text{C}_{26}\text{H}_{36}$
 $\text{GaS}^*\text{C}_4\text{H}_3\text{Cl}_2$
 $\text{GaS}^*\text{C}_7\text{H}_{19}$
 $\text{GaSi}^*\text{C}_4\text{H}_{11}\text{Br}_2$
 $\text{GaSi}^*\text{C}_4\text{H}_{11}\text{Cl}_2$
 $\text{GaSi}^*\text{C}_8\text{H}_{21}$

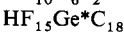
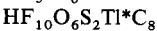
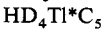
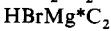
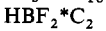
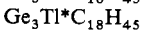
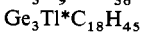
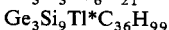
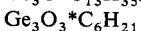
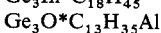
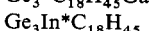
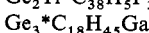
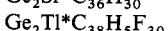
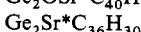
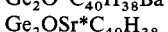
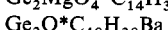
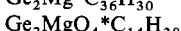
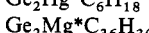
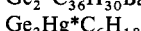
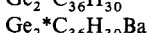
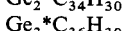
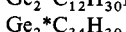
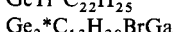
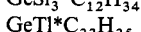
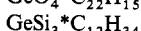
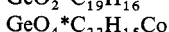
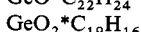
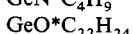
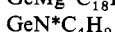
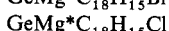
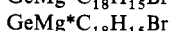
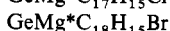
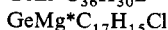
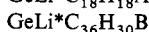
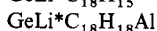
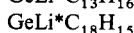
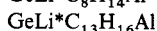
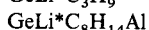
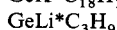
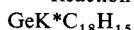


Formation: 5.3.4.4.1

Reaction with R₃B: 5.3.12.2.2Reaction with (R₂N)₂BX: 5.3.12.2.1

Reaction with chloroborazines:

5.3.12.2.1

Reaction with Na₂[C₂B₉H₁₁]: 5.3.12.3

Reaction with RBeX: 5.4.3.4.3

Reaction with BeX₂ and BeX₂: 5.4.3.3.2

- HMg*Br
 HMg*Br
 HMg*Cl
 HN*C
 HNa
 NaH
 Reaction with AlCl₃: 5.3.3.3
 HNa*C₂
 HO₃S*F
 H₂
 H₂
 Reaction with Al metal: 5.3.3.2.1
 H₂Al₂Cl₄*C
 H₂BCl₃*C₂
 H₂BF₃*C
 H₂B₂Cl₄*C₂
 H₂B₂F₄*C₂
 H₂B₄Cl₈*C₂
 H₂*Ba
 H₂*Be
 H₂*Be
 H₂BrCl₃In₂*C
 H₂*C₂
 H₂*Ca
 H₂Cl₂*C
 H₂Cl₂Hg*C₂
 H₂Cl₃In₃*C
 H₂Cl₄In₂*C
 H₂Cl₄Si*C
 H₂F₉O₆S₂Tl*C₈
 H₂F₁₀Ge*C₁₂
 H₂Hg
 HgH₂
 Decomposition: 5.3.3.4.4
 H₂I₂Mg₂*C
 H₂Mg
 MgH₂
 Active form: 5.4.2.4.3
 Addition to alkynes: 5.4.2.4.1
 Addition to olefins: 5.4.2.4.1
 Formation: 5.3.3.4.4
 Formation of active form: 5.4.2.4.1
 Reaction with LiAlPh₄: 5.4.2.4.3
 Reaction with ZnR₂: 5.4.2.4.3
 Reaction with LiR: 5.4.2.4.3
 Reaction with acidic hydrocarbons:
 5.4.2.4.2
 Reaction with amines and alcohols:
 5.4.2.4.2
 Reaction with cyclopentadiene: 5.4.2.4.2
 Redistribution with MgR₂: 5.4.2.4.3
 H₂N₂*C
 H₂N₂*C
 H₂N₂*C
 H₂O
 H₂O
 Reaction with RMgX: 5.4.2.5
 H₂Si*Cl₂
 H₂Sr
 SrH₂
 Reaction with C₅H₆: 5.4.3.4.2
 Reaction with olefins: 5.4.3.4.3
 H₂Zn
 ZnH₂
 Formation: 5.3.3.4.4
 H₃*Al
 H₃AlCl₂*C
 H₃AlCl₃Na*C
 H₃*B
 H₃BBr₂*C
 H₃BBr₂*C₂
 H₃B*C
 H₃BCl₂*C
 H₃BCl₂*C₂
 H₃BCl₂O₂*C
 H₃BCl₂S*C₄
 H₃BF₂*C
 H₃BF₂*C₂
 H₃BI₂*C
 H₃BO*C
 H₃B₂I₄MnO₃*C₈
 H₃B₉Br₈*C
 H₃BrMg*C
 H₃BrMg*C
 H₃BrMg*C
 H₃BrMg*C₂
 H₃BrMg*C₃
 H₃BrMgS*C₄
 H₃Br₂In*C
 H₃CaI*C
 H₃CaI*C
 H₃CaI*C
 H₃Cl*C
 H₃ClMg*C
 H₃Cl₂Ga*C
 H₃Cl₂Ga*C
 H₃Cl₂Ga*C₂
 H₃Cl₂GaS*C₄
 H₃Cl₂In*C
 H₃Cl₂Tl*C₂
 H₃Cl₃Ge*C
 H₃F₁₀O₆S₂Tl*C₉

$H_3F_{10}O_7S_2Ti^*C_9$	$H_4N^*C_4$
$H_3F_{12}Ti^*C_{18}$	$H_4N_2^*Ca$
H_3^*Ga	H_4Na^*Al
H_3GaO^*C	H_4Na^*Ga
H_3IMg^*C	$H_4O^*C_4$
$H_3ISSr^*C_4$	$H_4S^*C_4$
$H_3I_2In^*C$	$H_4S^*C_4$
$H_3I_2In^*C$	$H_5AlCl_2^*C_2$
$H_3I_3In_2^*C$	$H_5AlCl_2^*C_6$
H_3In^*C	$H_5BBr_2^*C_2$
H_3K^*Ge	$H_5BBr_2^*C_6$
H_3KSi	$H_5BCl_2^*C_2$
$K[SiH_3]$	$H_5BCl_2^*C_2$
Reaction with $H_2ClAl \cdot OEt_2$: 5.3.8.2.1	$H_5BCl_2^*C_3$
Reaction with R_2AlCl : 5.3.8.2.1	$H_5BCl_2^*C_6$
H_3Li^*C	$H_5BCl_2^*C_6$
$H_3Li^*C_3$	$H_5BCl_2^*C_6$
$H_3LiS^*C_4$	$H_5BF_2^*C_2$
$H_3O_3^*B$	$H_5BF_4N_2^*C_6$
H_3Si^*Cl	$H_5BI_2^*C_2$
$H_4BBr_2MnO_3^*C_8$	$H_5BI_2^*C_6$
$H_4BClF_4N_2^*C_6$	$H_5BI_2^*C_6$
$H_4BClN_2^*C_2$	$H_5BOS^*C_6$
$H_4BClO_2^*C_2$	$H_5BO_2^*C_2$
$H_4BI_2MnO_3^*C_8$	$H_5BO_2^*C_6$
$H_4B_2Br_4^*C_5$	$H_5BO_3^*C_4$
$H_4BaHg^*C_8$	$H_5B_2CoLi^*C_8$
H_4Be^*C	$H_5B_3^*C_2$
$H_4BrMgN^*C_5$	$H_5B_3^*C_2$
$H_4Br_2FIn^*C_6$	$H_5B_9Br_8^*C_2$
$H_4Br_2Mg_2^*C_3$	$H_5BeBr^*C_5$
$H_4Br_2Mg_2^*C_6$	$H_5BeCl^*C_2$
H_4^*C	$H_5BeCl^*C_3$
$H_4^*C_2$	$H_5BeF_6^*C_{11}$
$H_4^*C_2$	$H_5BeI^*C_5$
$H_4Cl_2Si^*C$	$H_5Br^*C_2$
$H_4Cl_3Ti^*C_2$	$H_5BrMg^*C_2$
$H_4Cl_4Ga_2^*C_2$	$H_5BrMg^*C_2$
$H_4IN^*C_3$	$H_5BrMg^*C_3$
$H_4I_2^*C_6$	$H_5BrMg^*C_3$
H_4K^*Ga	$H_5BrMg^*C_5$
H_4Li^*Al	$H_5BrMg^*C_6$
H_4Li^*Al	$H_5BrMg^*C_6$
H_4Li^*Al	$H_5Br_2Ga^*C_6$
H_4Li^*Al	$H_5Br_2In^*C_2$
H_4Li^*Al	$H_5Br_2In^*C_6$
$H_4Li_2^*C_6$	$H_5CaI^*C_2$
$H_4Li_2S^*C_3$	$H_5CaI^*C_6$
H_4Mg^*C	$H_5CaI^*C_8$
$H_4MgS^*C_3$	$H_5Cl^*C_2$
H_4MgZn	$H_5ClMg^*C_2$
$Mg[ZnH_4]$	$H_5ClMg^*C_3$
Formation: 5.4.2.4.3	

$H_5ClMg^*C_6$	$H_6BI^*C_2$
$H_5ClMgO^*C_2$	$H_6BI_2MnO_3^*C_9$
$H_5ClO^*C_7$	$H_6BI_3^*C_8$
$H_5Cl_2Ga^*C_2$	$H_6BN^*C_4$
$H_5Cl_2Ga^*C_6$	$H_6^*B_2$
$H_5Cl_2In^*C_6$	$H_6^*B_2$
$H_5Cl_2In^*C_6$	$H_6B_2^*C_4$
$H_5Cl_2Ti^*C_3$	$H_6B_2Cl_4^*C_3$
$H_5Cl_3Mg_2^*C_2$	$H_6B_3Sn^*C_2$
$H_5Cl_3Ti^*C_5$	$H_6B_4^*C_2$
$H_5F_3^*C_7$	$H_6B_4^*C_2$
$H_5F_{30}Ge_2Ti^*C_{38}$	$H_6B_4Pb^*C_2$
$H_5GaI_2^*C_6$	$H_6B_5Br_7^*C_2$
$H_5I^*C_6$	$H_6Ba^*C_2$
$H_5ISr^*C_6$	$H_6Be^*C_2$
$H_5I_2In^*C_2$	$H_6Be^*C_2$
$H_5I_2In^*C_5$	$H_6Be^*C_2$
$H_5I_2In^*C_6$	$H_6Be^*C_2$
$H_5In^*C_2$	$H_6Be^*C_2$
$H_5In^*C_5$	$H_6Be^*C_2$
H_5KZn_2	$H_6Be^*C_2$
$K[Zn_2H_5]$	$H_6Be^*C_6$
Formation: 5.3.3.4.4	$H_6Be^*C_6$
$H_5Li^*C_5$	$H_6Be^*C_6$
$H_5Li^*C_6$	$H_6BrIn^*C_2$
$H_5Li^*C_8$	$H_6Br_2Hg_2^*C_3$
H_5LiMg^*C	$H_6Br_2Mg_2^*C_3$
H_5LiMg_2	$H_6Br_2Mg_2^*C_3$
$LiMg_2H_5$	$H_6^*C_3$
Formation: 5.4.2.4.3	$H_6^*C_4$
$H_5MnO_3^*C_8$	$H_6^*C_5$
$H_5N^*C_5$	$H_6^*C_8$
$H_5Na^*C_5$	$H_6Ca^*C_2$
$H_5Na^*C_6$	$H_6Cd^*C_2$
H_5NaZn_2	$H_6ClGa^*C_2$
$Na[Zn_2H_5]$	$H_6ClIn^*C_2$
Formation: 5.3.3.4.4	$H_6ClTi^*C_4$
$H_5Ti^*C_5$	$H_6Cl_2Si^*C_2$
$H_6AlCl^*C_2$	$H_6Cl_2Sn^*C_2$
$H_6AlCl^*C_2$	$H_6Co_2O_6^*C_{10}$
$H_6AlF_2Na^*C_2$	$H_6CrO_3^*C_9$
$H_6AlN^*C_3$	$H_6F_6Sn^*C_6$
$H_6BBr^*C_2$	$H_6GaKN_2^*C_4$
$H_6BBr_2MnO_3^*C_9$	$H_6^*Ga_2$
$H_6BBr_3^*C_8$	$H_6Ga_2I_4^*C_2$
$H_6BCl^*C_2$	$H_6Hg^*C_2$
$H_6BCl^*C_4$	$H_6Hg^*C_2$
$H_6BClN_2^*C_3$	$H_6Hg^*C_2$
$H_6BClO_2^*C_2$	$H_6Hg^*C_4$
$H_6BClO_2^*C_2$	$H_6Hg^*C_4$
$H_6BCl_2N^*C_5$	$H_6Hg^*C_6$
$H_6BCl_3^*C_8$	$H_6IlIn^*C_2$

$H_6ITl^*C_2$	$H_7CaI^*C_9$
H_6K^*BGe	$H_7CaI^*C_{10}$
$H_6Li_2S^*C_4$	$H_7CaIO^*C_7$
$H_6Mg^*C_2$	$H_7ClMg^*C_3$
$H_6Mg^*C_2$	$H_7ClMg^*C_4$
$H_6Mg^*C_2$	$H_7ClMg^*C_7$
$H_6Mg^*C_4$	$H_7ClMg^*C_8$
$H_6Mg^*C_5$	$H_7ClMg^*C_9$
$H_6Mg^*C_6$	$H_7Cl_2Ga^*C_3$
$H_6Mg^*C_6$	$H_7Cl_2Mg^*C_4$
$H_6Mg^*C_6$	$H_7Cl_2Tl^*C_7$
$H_6MgS^*C_4$	$H_7F_6O_4Tl^*C_{11}$
$H_6Mg_2^*C$	$H_7GaO^*C_2$
$H_6N_2O_2^*C_4$	$H_7I^*C_7$
$H_6O_2^*C_2$	$H_7ISr^*C_7$
$H_6O_2^*C_7$	$H_7ISr^*C_{10}$
$H_6O_4Pb^*C_4$	$H_7I_2In^*C_3$
$H_6O_4S^*C_2$	$H_7InO_2^*C_2$
$H_6Sr^*C_2$	$H_7KZn^*C_2$
$H_6Zn^*C_2$	$H_7LiZn^*C_2$
$H_7Al^*C_2$	$H_7MgN^*C_5$
$H_7Al^*C_4$	$H_7MnO_3^*C_9$
$H_7BBr_2S^*C_2$	$H_7N^*C_8$
$H_7BCl_2^*C_3$	$H_7N_2Tl^*C_2$
$H_7BCl_2^*C_6$	$H_7NaZn^*C_2$
$H_7BCl_2S^*C_2$	$H_7Tl^*C_4$
$H_7BF_4N_2^*C_7$	$H_8AlN^*C_2$
$H_7BF_4N_2O^*C_7$	$H_8BBr^*C_7$
$H_7BIMnO_3^*C_9$	$H_8BBrS^*C_2$
$H_7BI_2S^*C_2$	$H_8BCl^*C_4$
$H_7BO_2^*C_3$	$H_8BClS^*C_2$
$H_7BO_2^*C_4$	$H_8BCl_2F_4Tl^*C_{12}$
$H_7BO_2S^*C_4$	$H_8BIS^*C_2$
$H_7BO_3^*C_6$	$H_8BLi^*C_6$
$H_7B_3^*C_2$	$H_8^*B_2Be$
$H_7B_3^*C_3$	$H_8B_2Br_4Fe^*C_{10}$
$H_7B_3O^*C$	$H_8B_2^*C$
$H_7B_3Si^*C_2$	$H_8B_2^*C_5$
$H_7B_4Na^*C_2$	$H_8B_2FeI_4^*C_{10}$
$H_7B_4Na^*C_2$	$H_8B_2I_2^*C_{12}$
$H_7B_4Na^*C_2$	$H_8B_4^*C_2$
$H_7B_4Na^*C_2$	$H_8B_4Cl_8^*C_{10}$
$H_7B_5^*C_2$	$H_8B_4FeO_3^*C_3$
$H_7BrMg^*C_3$	$H_8B_4O^*C$
$H_7BrMg^*C_5$	$H_8B_9Br_7^*C_3$
$H_7BrMg^*C_7$	$H_8B_{10}O_2^*C_2$
$H_7BrMg^*C_8$	$H_8Be^*C_6$
$H_7BrMg^*C_9$	$H_8Be^*C_7$
$H_7BrMg^*C_{10}$	$H_8BeCl_2^*C_{12}$
$H_7Br_2In^*C_3$	$H_8BrF_2In^*C_{12}$
$H_7Br_2In^*C_7$	$H_8Br_2FeMg_2^*C_{10}$
$H_7CaI^*C_3$	$H_8^*C_8$

H_8C_{10}	$H_9BeCl^*C_4$
$H_8Cl_2Si^*C_4$	$H_9BeLi^*C_3$
$H_8FeNa_2^*C_{10}$	$H_9BrGe^*C_3$
$H_8InN_2^*C_6$	$H_9BrMg^*C_4$
$H_8IN_2Ti^*C_6$	$H_9BrMg^*C_4$
$H_8K_2^*C_8$	$H_9BrMg^*C_6$
$H_8K_2^*C_8$	$H_9BrMg^*C_8$
$H_8Li^*B_5$	$H_9BrMg^*C_9$
$H_8Li_2Mg^*C_2$	$H_9BrMg^*C_{11}$
$H_8Mg^*C_3$	$H_9BrMg^*C_{14}$
$H_8Mg^*C_4$	$H_9BrMgO_2S^*C_9$
$H_8Mg^*C_8$	$H_9BrMgSn^*C_3$
$H_8MgO^*C_4$	$H_9BrSn^*C_3$
$H_8Mg_2^*C_6$	$H_9Br_2In^*C_4$
$H_8N_2^*C_{10}$	$H_9Br_3Ga_2^*C_3$
$H_8N_4^*B_{10}$	$H_9Br_3In_2^*C_3$
$H_8Na^*C_{10}$	$H_9CaI^*C_4$
$H_8Na^*C_{10}$	$H_9CaI^*C_{13}$
$H_8O^*C_7$	$H_9ClGe^*C_3$
$H_8Zn_2^*C_6$	$H_9ClMg^*C_4$
$H_9Al^*C_3$	$H_9ClMg^*C_4$
$H_9Al^*C_3$	$H_9ClMg^*C_4$
$H_9Al^*C_3$	$H_9ClMg^*C_4$
$H_9Al^*C_5$	$H_9ClMg^*C_5$
$H_9Al^*C_6$	$H_9ClMg^*C_7$
$H_9AlO_3^*C_3$	$H_9ClMg^*C_{11}$
$H_9Al_2Br_3^*C_3$	$H_9ClMg^*C_{11}$
$H_9Al_2Cl_3^*C_3$	$H_9ClMgPb^*C_3$
$H_9Al_2Cl_3^*C_3$	$H_9ClPb^*C_3$
$H_9Al_2I_3^*C_3$	$H_9ClSi^*C_3$
$H_9BBBr_3Fe^*C_{10}$	$H_9ClSi^*C_3$
$H_9B^*C_3$	$H_9ClSi^*C_3$
$H_9BCl^*C_9$	$H_9ClSn^*C_3$
$H_9BF_4N_2^*C_8$	$H_9Cl_2Ti^*C_8$
$H_9BF_4N_2O^*C_8$	$H_9CuO^*C_4$
$H_9BFeI_2^*C_{10}$	$H_9F_{12}O_3Ti^*C_{21}$
$H_9BIMnO_3^*C_{10}$	$H_9FeI^*C_{10}$
$H_9BIMnO_3^*C_{14}$	$H_9Ga^*C_3$
$H_9BI_2^*C_4$	$H_9Ga^*C_3$
$H_9BO_2^*C_3$	$H_9Ga^*C_3$
$H_9BO_2^*C_7$	$H_9Ga^*C_3$
$H_9BO_3^*C_3$	$H_9Ga^*C_6$
$H_9BO_3^*C_3$	$H_9Ga_2I_3^*C_3$
$H_9BS^*C_2$	$H_9GeLi^*C_3$
$H_9B_3^*C_5$	$H_9GeN^*C_4$
$H_9B_3Cl_3N_3^*C_3$	$H_9IMg^*C_4$
$H_9B_3O_6^*C_3$	$H_9I_3In^*C_4$
$H_9B_3Si^*C_3$	$H_9I_3In_2^*C_3$
$H_9^*B_5$	$H_9I_3In_2^*C_3$
$H_9^*B_5$	$H_9In^*C_3$
$H_9B_5^*C$	$H_9In^*C_3$
$H_9B_8Li^*C_2$	$H_9In^*C_3$

$H_9In^*C_3$	$H_{10}B_2I_2S^*C_6$
$H_9K^*C_9$	$H_{10}^*B_4$
$H_9Li^*C_4$	$H_{10}^*B_4$
$H_9LiO_2S^*C_9$	$H_{10}^*B_4$
$H_9LiPb^*C_3$	$H_{10}B_4Co_2Sn^*C_{16}$
$H_9LiSi^*C_3$	$H_{10}B_4Ge^*C_2$
$H_9LiSn^*C_3$	$H_{10}B_4Pb^*C_4$
$H_9LiSn^*C_3$	$H_{10}B_4Si^*C_2$
$H_9Mg_2N^*C_5$	$H_{10}B_4Sn^*C_4$
$H_9NPb^*C_4$	$H_{10}^*B_5BeBr$
$H_9NSi^*C_4$	$H_{10}B_5^*C_2$
$H_9NSn^*C_4$	$H_{10}B_5Cl_3Si^*C$
$H_9Na^*C_4$	$H_{10}^*B_6$
$H_9O_3P^*C_3$	$H_{10}B_{12}O_2^*C_2$
$H_9O_4Ti^*C_5$	$H_{10}Ba^*C_{12}$
$H_9O_6Ti^*C_6$	$H_{10}BaO_2^*C_4$
$H_9Ti^*C_3$	$H_{10}Be^*C_4$
$H_9Ti^*C_3$	$H_{10}Be^*C_4$
$H_9Ti^*C_3$	$H_{10}Be^*C_4$
$H_9Ti^*C_5$	$H_{10}Be^*C_4$
$H_{10}AlBr^*C_4$	$H_{10}Be^*C_6$
$H_{10}AlCl^*C_4$	$H_{10}Be^*C_7$
$H_{10}AlCl^*C_4$	$H_{10}Be^*C_{10}$
$H_{10}AlCl^*C_4$	$H_{10}Be^*C_{10}$
$H_{10}AlCl^*C_4$	$H_{10}Be^*C_{11}$
$H_{10}AlCl^*C_4$	$H_{10}Be^*C_{12}$
$H_{10}AlCl^*C_4$	$H_{10}Be^*C_{12}$
$H_{10}AlClF_2Sn^*C_4$	$H_{10}Be^*C_{12}$
$H_{10}AlCl_2K^*C_4$	$H_{10}Be^*C_{16}$
$H_{10}AlI^*C_4$	$H_{10}BeO_2^*C_4$
$H_{10}AlLiZn^*C_2$	$H_{10}BeS_2^*C_4$
$H_{10}AlN^*C_5$	$H_{10}BrGa^*C_{12}$
$H_{10}BBr^*C_4$	$H_{10}BrIn^*C_{12}$
$H_{10}BBr^*C_{12}$	$H_{10}BrMgN^*C_8$
$H_{10}BBrF_4^*C_{12}$	$H_{10}Br_2Mg_2^*C_5$
$H_{10}BCl^*C_4$	$H_{10}^*C_6$
$H_{10}BCl^*C_4$	$H_{10}^*C_{14}$
$H_{10}BCl^*C_5$	$H_{10}^*C_{16}$
$H_{10}BCl^*C_{12}$	$H_{10}Ca^*C_{10}$
$H_{10}BClF_4^*C_{12}$	$H_{10}Ca^*C_{10}$
$H_{10}BCIN^*C_4$	$H_{10}Ca^*C_{12}$
$H_{10}BCIN_2^*C_4$	$H_{10}Ca^*C_{16}$
$H_{10}BClO^*C_4$	$H_{10}CaO_2^*C_4$
$H_{10}BF_3O^*C_4$	$H_{10}Cd^*C_4$
$H_{10}BF_4I^*C_{12}$	$H_{10}Cd^*C_{12}$
$H_{10}BF_4Ti^*C_{12}$	$H_{10}ClGa^*C_4$
$H_{10}BI^*C_4$	$H_{10}ClGa^*C_{12}$
$H_{10}BI^*C_{12}$	$H_{10}ClIn^*C_4$
$H_{10}BI_3^*C_6$	$H_{10}ClIn^*C_{12}$
$H_{10}B_2^*C_2$	$H_{10}ClTi^*C_6$
$H_{10}B_2^*C_6$	$H_{10}ClTi^*C_{12}$
$H_{10}B_2Cl_4^*C_6$	$H_{10}Cl_2Ti^*C_4$

$H_{10}Cl_2Ti^*C_{10}$	$H_{10}Zn^*C_4$
$H_{10}Cl_2Ti^*C_{10}$	$H_{10}Zn^*C_{12}$
$H_{10}Cl_2Ti^*C_{10}$	$H_{10}Zn^*C_{12}$
$H_{10}Cl_2Zr^*C_{10}$	$H_{11}Al^*C_4$
$H_{10}Co^*C_{10}$	$H_{11}Al^*C_8$
$H_{10}D_3ClZr^*C_5$	$H_{11}Al^*C_{12}$
$H_{10}F_{15}GaO^*C_{22}$	$H_{11}AlO^*C_4$
$H_{10}F_{15}InO^*C_{22}$	$H_{11}BBr_2^*C_{13}$
$H_{10}Fe^*C_{10}$	$H_{11}B^*C_4$
$H_{10}GaI^*C_4$	$H_{11}B^*C_{12}$
$H_{10}GaI^*C_{12}$	$H_{11}BCl_2O^*C_4$
$H_{10}Ga_2I_4^*C_4$	$H_{11}BiMnO_3^*C_{15}$
$H_{10}Hg^*C_4$	$H_{11}BO^*C_4$
$H_{10}Hg^*C_4$	$H_{11}BO^*C_5$
$H_{10}Hg^*C_6$	$H_{11}BO^*C_{12}$
$H_{10}Hg^*C_6$	$H_{11}BOS^*C_4$
$H_{10}Hg^*C_{10}$	$H_{11}BO_2^*C_4$
$H_{10}Hg^*C_{12}$	$H_{11}BS^*C_4$
$H_{10}Hg^*C_{12}$	$H_{11}B_4Na^*C_4$
$H_{10}Hg^*C_{16}$	$H_{11}B_4Na^*C_4$
$H_{10}In^*C_4$	$H_{11}^*B_5$
$H_{10}In^*C_{10}$	$H_{11}B_5^*C$
$H_{10}In^*C_{12}$	$H_{11}B_9^*C_2$
$H_{10}IMgN^*C_8$	$H_{11}B_9^*C_2$
$H_{10}ITl^*C_4$	$H_{11}B_9Ge^*C_2$
$H_{10}LiN^*C_8$	$H_{11}B_9Na^*C_2$
$H_{10}LiP^*C_4$	$H_{11}B_9Na_2^*C_2$
$H_{10}Mg^*C_4$	$H_{11}B_9Pb^*C_2$
$H_{10}Mg^*C_4$	$H_{11}B_9Sn^*C_2$
$H_{10}Mg^*C_4$	$H_{11}B_{10}Na^*C$
$H_{10}Mg^*C_4$	$H_{11}BeBr^*C_5$
$H_{10}Mg^*C_4$	$H_{11}BeBrO_2^*C_5$
$H_{10}Mg^*C_4$	$H_{11}BeClN_2^*C_{12}$
$H_{10}Mg^*C_5$	$H_{11}BeClO_2^*C_5$
$H_{10}Mg^*C_{10}$	$H_{11}BeN^*C_7$
$H_{10}Mg^*C_{10}$	$H_{11}BeNa^*C_4$
$H_{10}Mg^*C_{12}$	$H_{11}BrMg^*C_5$
$H_{10}Mg^*C_{12}$	$H_{11}BrMg^*C_6$
$H_{10}Mg^*C_{12}$	$H_{11}BrMg^*C_9$
$H_{10}Mg^*C_{12}$	$H_{11}BrMg^*C_{13}$
$H_{10}Mg^*C_{12}$	$H_{11}BrMgO_2S^*C_{14}$
$H_{10}Mg^*C_{14}$	$H_{11}BrMgSi^*C_5$
$H_{10}MgO^*C_9$	$H_{11}Br_2GaSi^*C_4$
$H_{10}N_2^*C_{13}$	$H_{11}ClGaN^*C_3$
$H_{10}O^*C_4$	$H_{11}ClMg^*C_5$
$H_{10}O^*C_8$	$H_{11}ClMg^*C_5$
$H_{10}O_2Sr^*C_4$	$H_{11}ClMg^*C_6$
$H_{10}O_2Zn^*C_4$	$H_{11}ClMg^*C_7$
$H_{10}S^*C_4$	$H_{11}ClMg^*C_9$
$H_{10}Si^*C_3$	$H_{11}ClMgSi^*C_4$
$H_{10}Sn^*C_{10}$	$H_{11}ClSi^*C_4$
$H_{10}Sn^*C_{12}$	$H_{11}ClSi^*C_4$

$H_{11}Cl_2GaSi^*C_4$	$H_{12}Cl_3GaSn^*C_4$
$H_{11}Cl_2InSi^*C_4$	$H_{12}Cl_3In^*C_{18}$
$H_{11}Ga^*C_4$	$H_{12}Cl_4O_4Si_4^*C_4$
$H_{11}Ga^*C_7$	$H_{12}D_2GaN^*C_4$
$H_{11}In^*C_7$	$H_{12}F_3Ga^*C_{18}$
$H_{11}K^*C_{13}$	$H_{12}F_3In^*C_{18}$
$H_{11}Li^*C_8$	$H_{12}GaI^*C_5$
$H_{11}LiO_2S^*C_{14}$	$H_{12}GaK^*C_4$
$H_{11}LiSi^*C_8$	$H_{12}GaLi^*C_4$
$H_{11}N^*C_8$	$H_{12}GaN^*C_3$
$H_{11}Tl^*C_7$	$H_{12}GaN^*C_3$
$H_{11}Tl^*C_{10}$	$H_{12}Ge^*C_4$
$H_{12}AlClO^*C_4$	$H_{12}Hg_2^*C_5$
$H_{12}AlI^*C_5$	$H_{12}LiTl^*C_4$
$H_{12}AlLi^*C_8$	$H_{12}Li_2Zn^*C_4$
$H_{12}AlLi^*C_8$	$H_{12}Mg^*C_5$
$H_{12}AlLi^*C_{12}$	$H_{12}Mg^*C_6$
$H_{12}AlN^*C_3$	$H_{12}Mg^*C_8$
$H_{12}AlNa^*C_4$	$H_{12}MgN_2^*C_{10}$
$H_{12}AlNa^*C_4$	$H_{12}MgN_2^*C_{16}$
$H_{12}AlNa^*C_6$	$H_{12}MgZn^*C_4$
$H_{12}AlNaO_4^*C_{16}$	$H_{12}MgZn^*C_4$
$H_{12}AlNaS_4^*C_{16}$	$H_{12}N_2^*C_5$
$H_{12}BCl^*C_6$	$H_{12}N_2Sn^*C_4$
$H_{12}BCIN_2^*C_4$	$H_{12}Na_2^*C_8$
$H_{12}BCIN_2^*C_4$	$H_{12}S_4Sn^*C_{16}$
$H_{12}BCIO^*C_4$	$H_{12}Si^*C_4$
$H_{12}BCIO^*C_4$	$H_{12}Si^*C_5$
$H_{12}BCl_3^*C_{18}$	$H_{12}Si^*C_6$
$H_{12}BFeI^*C_{11}$	$H_{12}Si^*C_7$
$H_{12}BLiSn^*C_3$	$H_{12}Sn^*C_4$
$H_{12}B_2^*C_3$	$H_{12}Sn^*C_4$
$H_{12}B_2F_2^*C_8$	$H_{12}Sn^*C_8$
$H_{12}B_2O_4^*C_4$	$H_{13}Al^*C_7$
$H_{12}B_4^*C$	$H_{13}Al^*C_{18}$
$H_{12}B_4^*C_2$	$H_{13}AlO^*C_4$
$H_{12}B_6^*C_4$	$H_{13}AlO^*C_{10}$
$H_{12}^*B_8$	$H_{13}B^*C_6$
$H_{12}B_8FeSn^*C_8$	$H_{13}B^*C_{10}$
$H_{12}B_{10}^*C_2$	$H_{13}BCl_2^*C_6$
$H_{12}Be^*C_5$	$H_{13}BO_2^*C_6$
$H_{12}BeLi_2^*C_4$	$H_{13}B_3Be^*C_5$
$H_{12}BeN_2^*C_4$	$H_{13}B_3O^*C_2$
$H_{12}BrMgNO^*C_{12}$	$H_{13}B_5Be^*C$
$H_{12}Br_2Mg_2O^*C_6$	$H_{13}B_5Be^*C_5$
$H_{12}Br_2Mg_2O^*C_7$	$H_{13}B_5^*C_3$
$H_{12}Br_3Ga^*C_{18}$	$H_{13}B_9O^*C$
$H_{12}Br_3In^*C_{18}$	$H_{13}B_{10}NNa_2^*C$
$H_{12}^*C_8$	$H_{13}BaIO^*C_6$
$H_{12}ClTi^*C_{13}$	$H_{13}BeClO_2^*C_{10}$
$H_{12}Cl_2Mg_2^*C_8$	$H_{13}BrMg^*C_{19}$
$H_{12}Cl_3Ga^*C_{18}$	$H_{13}BrSi^*C_{11}$

$H_{13}CaIO_2 \cdot C_{10}$	$H_{14}In \cdot C_{14}$
$H_{13}ClMg \cdot C_7$	$H_{14}Mg \cdot C_6$
$H_{13}ClMgO_2 \cdot C_7$	$H_{14}Mg \cdot C_6$
$H_{13}ClZr \cdot C_{11}$	$H_{14}Mg \cdot C_6$
$H_{13}FMg \cdot C_6$	$H_{14}Mg \cdot C_{12}$
$H_{13}IMg \cdot B_{10}$	$H_{14}Mg \cdot C_{18}$
$H_{13}IMg \cdot B_{10}$	$H_{14}MgO_4 \cdot C_6$
$H_{13}IMg \cdot C_{19}$	$H_{14}MgSi \cdot C_9$
$H_{13}IMg \cdot C_{20}$	$H_{14}Si \cdot C_5$
$H_{13}Li \cdot C_{20}$	$H_{14}Si \cdot C_9$
$H_{13}Na \cdot B_{10}$	$H_{14}Si \cdot C_9$
$H_{13}O_2Ti \cdot C_6$	$H_{14}Si \cdot C_{14}$
$H_{14}AlGeLi \cdot C_8$	$H_{14}Sn \cdot C_{12}$
$H_{14}AlN \cdot C_4$	$H_{14}Sr \cdot C_{14}$
$H_{14}AlN \cdot C_{11}$	$H_{15}Al \cdot C_6$
$H_{14}AlN \cdot C_{14}$	$H_{15}Al \cdot C_6$
$H_{14}AlNa \cdot C_{12}$	$H_{15}Al \cdot C_6$
$H_{14}Al_2Na \cdot C_4$	$H_{15}Al \cdot C_6$
$H_{14}BBr_2ClS \cdot C_7$	$H_{15}Al \cdot C_6$
$H_{14}BCl \cdot C_6$	$H_{15}Al \cdot C_6$
$H_{14}BF_4O_2Ti \cdot C_{14}$	$H_{15}Al \cdot C_6$
$H_{14}BF_4Ti \cdot C_{14}$	$H_{15}Al \cdot C_6$
$H_{14}BF_4FeI \cdot C_{16}$	$H_{15}Al \cdot C_6$
$H_{14}BN \cdot C_5$	$H_{15}Al \cdot C_6$
$H_{14}B_2Be_2 \cdot C_2$	$H_{15}Al \cdot C_6$
$H_{14}B_2 \cdot C_4$	$H_{15}Al \cdot C_6$
$H_{14}B_2 \cdot C_{12}$	$H_{15}Al \cdot C_9$
$H_{14}B_2O_4 \cdot C_5$	$H_{15}Al \cdot C_{10}$
$H_{14}B_2O_4 \cdot C_5$	$H_{15}Al \cdot C_{18}$
$H_{14}B_9Li \cdot C_3$	$H_{15}Al \cdot C_{18}$
$H_{14} \cdot B_{10}$	$H_{15}Al \cdot C_{18}$
$H_{14}B_{10}Ge \cdot C_2$	$H_{15}Al \cdot C_{20}$
$H_{14}B_{10}O \cdot C_4$	$H_{15}AlMg \cdot C_5$
$H_{14}B_{10}OS \cdot C_3$	$H_{15}AlNaO_4 \cdot C_6$
$H_{14}Ba \cdot C_{14}$	$H_{15}AlO \cdot C_7$
$H_{14}Be \cdot C_6$	$H_{15}AlO_2Si \cdot C_4$
$H_{14}Be \cdot C_9$	$H_{15}Al_2Br_3 \cdot C_6$
$H_{14}Be \cdot C_{14}$	$H_{15}Al_2Br_3 \cdot C_9$
$H_{14}Be \cdot C_{20}$	$H_{15}Al_2Br_3 \cdot C_{18}$
$H_{14}BrIn \cdot C_{14}$	$H_{15}Al_2Cl_3 \cdot C_6$
$H_{14}BrIn \cdot C_{20}$	$H_{15}Al_2Cl_3 \cdot C_6$
$H_{14}BrInO_4 \cdot C_8$	$H_{15}Al_2Cl_3 \cdot C_{18}$
$H_{14}BrMgO \cdot C_9$	$H_{15}Al_2I_3 \cdot C_6$
$H_{14}Ca \cdot C_{14}$	$H_{15}Al_2I_3 \cdot C_{18}$
$H_{14}Ca \cdot C_{18}$	$H_{15}As \cdot C_5$
$H_{14}GaN \cdot C_4$	$H_{15}B \cdot C_6$
$H_{14}Ga_2 \cdot C_4$	$H_{15}B \cdot C_6$
$H_{14}Ga_2I_4 \cdot C_6$	$H_{15}B \cdot C_8$
$H_{14}Hg \cdot C_6$	$H_{15}B \cdot C_9$
$H_{14}Hg \cdot C_8$	$H_{15}B \cdot C_{11}$
$H_{14}Hg \cdot C_{14}$	$H_{15}B \cdot C_{18}$
$H_{14}Hg \cdot C_{20}$	$H_{15}B \cdot C_{18}$

$H_{15}BClN^*C_6$
 $H_{15}BCo^*C_{16}$
 $H_{15}BF_4O^*C_6$
 $H_{15}BN_2Sn^*C_6$
 $H_{15}BO^*C_7$
 $H_{15}BO^*C_{14}$
 $H_{15}BO^*C_{20}$
 $H_{15}BO_2^*C_7$
 $H_{15}BO_2^*C_9$
 $H_{15}BO_2^*C_{12}$
 $H_{15}BO_3^*C_6$
 $H_{15}BSi^*C_{12}$
 $H_{15}B_3Cl_3N_3^*C_{18}$
 $H_{15}B_3O_6^*C_{18}$
 $H_{15}B_4ClSi^*C_5$
 $H_{15}B_5Be^*C_5$
 $H_{15}B_5^*C_2$
 $H_{15}B_5^*C_7$
 $H_{15}B_7^*C_4$
 $H_{15}^*B_9$
 $H_{15}BaCl^*C_{19}$
 $H_{15}BeLi^*C_{18}$
 $H_{15}BeLiN^*C_6$
 $H_{15}BeLi_3^*C_5$
 $H_{15}BeN^*C_5$
 $H_{15}BeN^*C_9$
 $H_{15}Be_2Li^*C_5$
 $H_{15}Br^*C_{19}$
 $H_{15}BrGeMg^*C_{18}$
 $H_{15}BrMg^*C_{18}$
 $H_{15}BrMg^*C_{13}$
 $H_{15}BrMg^*C_{16}$
 $H_{15}BrMg^*C_{19}$
 $H_{15}BrMg^*C_{19}$
 $H_{15}BrMgPb^*C_{18}$
 $H_{15}BrMgPb^*C_{18}$
 $H_{15}BrMgSi^*C_{17}$
 $H_{15}BrMgSi^*C_{18}$
 $H_{15}BrMgSi^*C_{18}$
 $H_{15}BrMgSn^*C_{16}$
 $H_{15}BrMgSn^*C_{18}$
 $H_{15}BrPb^*C_6$
 $H_{15}Br_3Ga_2^*C_6$
 $H_{15}Br_3In_2^*C_6$
 $H_{15}^*C_{19}$
 $H_{15}CaCl^*C_{19}$
 $H_{15}CaI^*C_7$
 $H_{15}CaI^*C_{15}$
 $H_{15}CaI^*C_{19}$
 $H_{15}CaIO_2^*C_{11}$
 $H_{15}ClGe^*C_{18}$
 $H_{15}ClGeMg^*C_{17}$

$H_{15}ClGeMg^*C_{18}$
 $H_{15}ClMg^*C_{11}$
 $H_{15}ClMgPb^*C_6$
 $H_{15}ClMgPb^*C_{18}$
 $H_{15}ClSi^*C_6$
 $H_{15}ClSi^*C_{18}$
 $H_{15}ClSn^*C_{18}$
 $H_{15}Cl_2Ga^*C_7$
 $H_{15}CoGeO_4^*C_{22}$
 $H_{15}CoO_4Si^*C_{21}$
 $H_{15}CoO_4Si^*C_{22}$
 $H_{15}DGaN^*C_5$
 $H_{15}DGe^*C_{18}$
 $H_{15}F_6O_5Ti^*C_{11}$
 $H_{15}F_{15}InP^*C_{36}$
 $H_{15}Ga^*C_6$
 $H_{15}Ga^*C_9$
 $H_{15}Ga^*C_{18}$
 $H_{15}Ga_2I_3^*C_6$
 $H_{15}GeK^*C_{18}$
 $H_{15}GeLi^*C_{18}$
 $H_{15}IMg^*C_{19}$
 $H_{15}I_3In_2^*C_6$
 $H_{15}In^*C_6$
 $H_{15}In^*C_6$
 $H_{15}In^*C_9$
 $H_{15}In^*C_{15}$
 $H_{15}In^*C_{18}$
 $H_{15}In^*C_{18}$
 $H_{15}KSi^*C_{18}$
 $H_{15}KSi^*C_{18}$
 $H_{15}Li^*C_8$
 $H_{15}Li^*C_{16}$
 $H_{15}LiSi^*C_{18}$
 $H_{15}LiSi^*C_{18}$
 $H_{15}LiSi^*C_{18}$
 $H_{15}LiSn^*C_6$
 $H_{15}N^*C_{11}$
 $H_{15}NSi^*C_8$
 $H_{15}Na^*C_{19}$
 $H_{15}O_2Ti^*C_7$
 $H_{15}O_2Ti^*C_{11}$
 $H_{15}Ti^*C_6$
 $H_{15}Ti^*C_6$
 $H_{15}Ti^*C_6$
 $H_{15}Ti^*C_{15}$
 $H_{15}Ti^*C_{18}$
 $H_{16}AlGeLi^*C_{13}$
 $H_{16}AlK^*C_{10}$
 $H_{16}AlN^*C_5$
 $H_{16}AlN^*C_5$
 $H_{16}AlN^*C_{14}$

$H_{16}AlNa^*C_6$	$H_{17}BCl_2^*C_8$
$H_{16}AlNa^*C_6$	$H_{17}BO^*C_9$
$H_{16}B^*C_{12}$	$H_{17}BO^*C_{12}$
$H_{16}BN^*C_{11}$	$H_{17}BO_2^*C_8$
$H_{16}BN^*C_{14}$	$H_{17}BO_2^*C_{13}$
$H_{16}BN^*C_{17}$	$H_{17}BO_3^*C_8$
$H_{16}BNO^*C_{14}$	$H_{17}B_5^*C_4$
$H_{16}BNa^*C_6$	$H_{17}B_5Pb^*C_3$
$H_{16}B_2O_4^*C_6$	$H_{17}B_5Sn^*C_3$
$H_{16}B_4^*C_8$	$H_{17}B_{10}NO^*C_4$
$H_{16}B_4^*C_{10}$	$H_{17}BrMg^*C_9$
$H_{16}B_4Ge^*C_5$	$H_{17}CaIN_2^*C_{12}$
$H_{16}B_4Pb^*C_5$	$H_{17}ClMgOSi^*C_7$
$H_{16}B_4Si^*C_5$	$H_{17}ClOSi^*C_7$
$H_{16}B_4Si^*C_5$	$H_{17}O_2Ti^*C_8$
$H_{16}B_4Sn^*C_5$	$H_{18}AlCl^*C_8$
$H_{16}B_5ClSi^*C_3$	$H_{18}AlCl^*C_8$
$H_{16}^*B_6Be$	$H_{18}AlD^*C_8$
$H_{16}B_8^*C_4$	$H_{18}AlGeLi^*C_{18}$
$H_{16}B_8Si^*C_4$	$H_{18}AlLiSi^*C_{18}$
$H_{16}B_8Si^*C_4$	$H_{18}AlLiSn^*C_6$
$H_{16}B_{10}^*C$	$H_{18}AlN^*C_6$
$H_{16}B_{10}^*C$	$H_{18}AlN^*C_9$
$H_{16}BaN^*C_{16}$	$H_{18}AlN^*C_9$
$H_{16}BeN_2O^*C_{12}$	$H_{18}AlN^*C_9$
$H_{16}Be_2^*C_6$	$H_{18}AlN^*C_{12}$
$H_{16}^*C_{10}$	$H_{18}AlNa^*C_{12}$
$H_{16}CaN^*C_{16}$	$H_{18}Al_2^*C_6$
$H_{16}Cl_2Mg_2^*C_{16}$	$H_{18}Al_2^*C_6$
$H_{16}GaN^*C_5$	$H_{18}Al_2^*C_{10}$
$H_{16}Ge^*C_6$	$H_{18}BBr^*C_8$
$H_{16}Ge^*C_{17}$	$H_{18}BCl^*C_8$
$H_{16}Ge^*C_{18}$	$H_{18}BCl^*C_{10}$
$H_{16}Ge^*C_{18}$	$H_{18}BF_4O_2Ti^*C_{16}$
$H_{16}GeO_2^*C_{19}$	$H_{18}BF_4Ti^*C_{16}$
$H_{16}Li^*C_8$	$H_{18}BI^*C_{10}$
$H_{16}Mg^*C_{10}$	$H_{18}BK^*C_8$
$H_{16}Mg^*C_{16}$	$H_{18}BN_3^*C_6$
$H_{16}NSr^*C_{16}$	$H_{18}BNa^*C_9$
$H_{16}N_4^*C_{10}$	$H_{18}B_2^*C_6$
$H_{16}Na_2^*C_{16}$	$H_{18}B_2^*C_8$
$H_{16}Si^*C_6$	$H_{18}B_2O_6^*C_9$
$H_{16}Si^*C_9$	$H_{18}B_{10}^*C_2$
$H_{16}SiSn^*C_8$	$H_{18}B_{10}^*C_3$
$H_{16}Sn^*C_6$	$H_{18}B_{10}^*C_6$
$H_{16}Sn^*C_6$	$H_{18}B_{10}Ge^*C_2$
$H_{16}Sn^*C_{18}$	$H_{18}B_{10}N_2^*C_4$
$H_{17}AlO^*C_7$	$H_{18}B_{10}O_2^*C_8$
$H_{17}AlO^*C_{10}$	$H_{18}B_{10}S^*C_2$
$H_{17}BBr_2S^*C_8$	$H_{18}B_{10}Sn^*C_2$
$H_{17}B^*C_8$	$H_{18}Ba^*C_{26}$
$H_{17}B^*C_9$	$H_{18}Be^*C_8$

$H_{18}Be^*C_{14}$	$H_{19}AlSn^*C_7$
$H_{18}Be^*C_{16}$	$H_{19}BBr_2S^*C_8$
$H_{18}BeO_2^*C_8$	$H_{19}B^*C_9$
$H_{18}BeS_2^*C_8$	$H_{19}B^*C_{10}$
$H_{18}Be_2^*C_{24}$	$H_{19}B^*C_{11}$
$H_{18}BrGa^*C_8$	$H_{19}B^*C_{14}$
$H_{18}Ca^*C_8$	$H_{19}BCINSn^*C_7$
$H_{18}ClGa^*C_8$	$H_{19}BLi^*C_9$
$H_{18}ClMg^*C_{10}$	$H_{19}BN_2Pb^*C_7$
$H_{18}ClSi_2Ti^*C_6$	$H_{19}BO^*C_{16}$
$H_{18}GaLiSn^*C_6$	$H_{19}BO_2^*C_8$
$H_{18}GaN^*C_6$	$H_{19}BO_2^*C_{10}$
$H_{18}GaN^*C_6$	$H_{19}B_3O_6^*C_7$
$H_{18}Ga_2I_4^*C_8$	$H_{19}B_5^*C_4$
$H_{18}Ga_2K_2^*C_6$	$H_{19}BeBrO_2^*C_8$
$H_{18}Ge^*C_{10}$	$H_{19}BeClO_2^*C_8$
$H_{18}Ge_2Hg^*C_6$	$H_{19}BrMgN_2^*C_7$
$H_{18}Hg^*C_8$	$H_{19}BrMgSn^*C_{18}$
$H_{18}HgSi_2^*C_6$	$H_{19}Ga^*C_8$
$H_{18}HgSi_2^*C_6$	$H_{19}Ga^*C_{10}$
$H_{18}HgSi_2^*C_6$	$H_{19}GaO^*C_7$
$H_{18}HgSn_2^*C_6$	$H_{19}GaS^*C_7$
$H_{18}InLiSn^*C_6$	$H_{19}IO_2Sr^*C_9$
$H_{18}LiN^*C_9$	$H_{19}InO^*C_7$
$H_{18}LiSnTi^*C_6$	$H_{19}LiSi_2^*C_7$
$H_{18}Mg^*C_8$	$H_{20}AlCa^*C_8$
$H_{18}Mg^*C_8$	$H_{20}AlLi^*C_{24}$
$H_{18}Mg^*C_8$	$H_{20}AlLi^*C_{32}$
$H_{18}Mg^*C_8$	$H_{20}AlLiSi^*C_{11}$
$H_{18}Mg^*C_{14}$	$H_{20}AlN^*C_7$
$H_{18}MgO_2^*C_{12}$	$H_{20}AlN^*C_{29}$
$H_{18}Mg_3O_3^*C_9$	$H_{20}AlNa^*C_8$
$H_{18}N_3OP^*C_6$	$H_{20}AlNa^*C_{24}$
$H_{18}O^*C_8$	$H_{20}AlSr^*C_8$
$H_{18}OSi_2^*C_6$	$H_{20}AsCl_3Sn^*C_{24}$
$H_{18}O_2^*B_{12}$	$H_{20}BBa^*C_8$
$H_{18}Si^*C_8$	$H_{20}BCa^*C_8$
$H_{18}Si_2^*C_6$	$H_{20}BCIN_2^*C_8$
$H_{18}Sn_2^*C_6$	$H_{20}BCIS^*C_8$
$H_{18}Sn_2^*C_6$	$H_{20}BNa^*C_{24}$
$H_{18}Sn_2^*C_6$	$H_{20}BSr^*C_8$
$H_{18}Sr^*C_{26}$	$H_{20}B_4Ge^*C_7$
$H_{18}Zn^*C_8$	$H_{20}B_4Si^*C_7$
$H_{19}Al^*C_8$	$H_{20}B_{10}^*C_7$
$H_{19}Al^*C_{10}$	$H_{20}B_{10}Si^*C$
$H_{19}Al^*C_{17}$	$H_{20}B_{17}Li^*C_4$
$H_{19}Al^*C_{24}$	$H_{20}BaHg^*C_{32}$
$H_{19}AlO^*C_7$	$H_{20}BaZn^*C_8$
$H_{19}AlO^*C_8$	$H_{20}BaZn^*C_8$
$H_{19}AlO^*C_{10}$	$H_{20}BeLi_2^*C_{32}$
$H_{19}AlO^*C_{11}$	$H_{20}BeO^*C_{20}$
$H_{19}AlO^*C_{13}$	$H_{20}Be_2FK^*C_8$

$H_{20}Be_2N_2C_6$	$H_{21}GaO^*C_{21}$
$H_{20}BrMgN^*C_8$	$H_{21}GaO_3^*C_{21}$
$H_{20}CaZn^*C_8$	$H_{21}GaSi^*C_8$
$H_{20}F_{20}NTl^*C_{32}$	$H_{21}Ge_3O_3^*C_6$
$H_{20}GaK^*C_8$	$H_{21}IO_3Sr^*C_{10}$
$H_{20}GaLi^*C_8$	$H_{21}I_3In_2^*C_9$
$H_{20}InP^*C_7$	$H_{21}In^*C_9$
$H_{20}Li_2^*C_{28}$	$H_{21}In^*C_9$
$H_{20}MgN_2^*C_{14}$	$H_{21}In^*C_{18}$
$H_{20}MgN_2^*C_{22}$	$H_{21}In^*C_{21}$
$H_{20}Mg_2^*C_{10}$	$H_{21}In^*C_{27}$
$H_{20}N_2O_2S^*C_8$	$H_{21}InO_3^*C_{21}$
$H_{20}O_4Ti^*C_8$	$H_{21}LiMg_2^*C_8$
$H_{20}Pb^*C_8$	$H_{21}O_5Ti^*C_{11}$
$H_{20}Pb^*C_{24}$	$H_{21}O_6Ti^*C_{12}$
$H_{20}Si^*C_8$	$H_{21}SnTi^*C_8$
$H_{20}Sn^*C_8$	$H_{21}SnTi^*C_{20}$
$H_{20}Sn^*C_{12}$	$H_{22}AlN^*C_{25}$
$H_{20}Sn^*C_{24}$	$H_{22}AlN^*C_{25}$
$H_{20}Sn^*C_{24}$	$H_{22}BKO_3^*C_9$
$H_{20}SrZn^*C_8$	$H_{22}BNO^*C_{16}$
$H_{21}Al^*C_9$	$H_{22}B_2^*C_8$
$H_{21}Al^*C_{12}$	$H_{22}B_2^*C_{10}$
$H_{21}Al^*C_{21}$	$H_{22}B_4^*C_{12}$
$H_{21}AlClKSi^*C_8$	$H_{22}B_6Be_2^*C_2$
$H_{21}AlSi^*C_8$	$H_{22}B_6Si^*C_5$
$H_{21}AlSi^*C_{12}$	$H_{22}B_8^*C_8$
$H_{21}Al_3^*C_8$	$H_{22}B_{10}^*C_4$
$H_{21}B^*C_9$	$H_{22}B_{10}N_2^*C_6$
$H_{21}B^*C_{12}$	$H_{22}B_{10}Si^*C_3$
$H_{21}B^*C_{21}$	$H_{22}^*B_{18}$
$H_{21}B^*C_{30}$	$H_{22}B_{20}Hg^*C_4$
$H_{21}BN_2Si^*C_7$	$H_{22}Be^*C_{10}$
$H_{21}BO^*C_9$	$H_{22}Be^*C_{16}$
$H_{21}BO^*C_{13}$	$H_{22}Be^*C_{18}$
$H_{21}BO_2^*C_{10}$	$H_{22}BeClN^*C_{11}$
$H_{21}BO_2^*C_{11}$	$H_{22}BeN_2O^*C_{15}$
$H_{21}BO_2^*C_{12}$	$H_{22}BeSi_2^*C_8$
$H_{21}B_3^*C_{12}$	$H_{22}BrGaSi_2^*C_8$
$H_{21}B_8FeNa^*C_8$	$H_{22}BrMgSi^*C_{17}$
$H_{21}B_9BeO^*C_6$	$H_{22}Ca^*C_{26}$
$H_{21}BeBrN_2^*C_8$	$H_{22}ClGaSi_2^*C_8$
$H_{21}BeLi^*C_{21}$	$H_{22}ClInSi_2^*C_8$
$H_{21}BrIn^*C_{27}$	$H_{22}Ga_2^*C_{20}$
$H_{21}Br_2InN_2^*C_8$	$H_{22}Hg^*C_{10}$
$H_{21}Br_3In_2^*C_9$	$H_{22}HgSi_2^*C_8$
$H_{21}CaIO_2^*C_{13}$	$H_{22}HgSi_2^*C_{16}$
$H_{21}Ga^*C_9$	$H_{22}In_2^*C_{20}$
$H_{21}Ga^*C_{10}$	$H_{22}Mg^*C_{10}$
$H_{21}Ga^*C_{21}$	$H_{22}Mg^*C_{16}$
$H_{21}Ga^*C_{27}$	$H_{22}Mg^*C_{18}$
$H_{21}GaN_2^*C_8$	$H_{22}MgSi_2^*C_8$

$H_{22}MgSi_2 * C_{16}$	$H_{25}BO * C_{11}$
$H_{22}O * C_{10}$	$H_{25}BO * C_{15}$
$H_{22}Pb * C_{25}$	$H_{25}BO_2 * C_{12}$
$H_{22}Si * C_{11}$	$H_{25}BO_2 * C_{16}$
$H_{22}Si_2 * C_{11}$	$H_{25}BO_2 * C_{17}$
$H_{22}Sn_2 * C_{12}$	$H_{25}BeNa * C_{31}$
$H_{23}Al * C_{13}$	$H_{25}CaClO_2 * C_{21}$
$H_{23}Al * C_{14}$	$H_{25}GaLi_2 * C_{10}$
$H_{23}AlO * C_{10}$	$H_{25}GaO * C_{10}$
$H_{23}B * C_{10}$	$H_{25}GeTi * C_{22}$
$H_{23}B * C_{12}$	$H_{25}IO_2Sr * C_{12}$
$H_{23}B * C_{13}$	$H_{25}Mg * C_{19}$
$H_{23}B * C_{14}$	$H_{25}Sb * C_{10}$
$H_{23}BCl_2S * C_{10}$	$H_{26}AlClZr * C_{18}$
$H_{23}BO * C_{14}$	$H_{26}AlN * C_{10}$
$H_{23}BO_2 * C_{14}$	$H_{26}BCl * C_{12}$
$H_{23}BO_2 * C_{14}$	$H_{26}BI * C_{12}$
$H_{23}B_{10}Sn * C_{12}$	$H_{26}B_2 * C_{12}$
$H_{23}BeN * C_9$	$H_{26}B_2Sn * C_{26}$
$H_{23}IO_2Sr * C_{11}$	$H_{26}BeN_2 * C_{10}$
$H_{24}AlN * C_9$	$H_{26}BeO_2 * C_{10}$
$H_{24}AlN * C_{27}$	$H_{26}BeO_2 * C_{14}$
$H_{24}Al_2Be * C_8$	$H_{26}BeO_2 * C_{24}$
$H_{24}Al_2Be * C_{16}$	$H_{26}Be_2N_2 * C_8$
$H_{24}Al_2Mg * C_8$	$H_{26}CaO_2 * C_{18}$
$H_{24}AsGa * C_8$	$H_{26}CaO_2 * C_{20}$
$H_{24}B_2 * C_{12}$	$H_{26}Mg * C_{12}$
$H_{24}B_2N_4 * C_8$	$H_{26}Mg * C_{20}$
$H_{24}B_2O_4 * C_{10}$	$H_{26}MgOSi_2 * C_{10}$
$H_{24}B_4O_8 * C_9$	$H_{27}Al * C_{12}$
$H_{24}B_4Si_2 * C_8$	$H_{27}Al * C_{12}$
$H_{24}B_{10}S_2 * C_4$	$H_{27}AlCa * C_{17}$
$H_{24}Ba * C_{28}$	$H_{27}AlCl_2Si_3 * C_{10}$
$H_{24}BeO_2 * C_9$	$H_{27}AlO * C_{12}$
$H_{24}Be_2N_2 * C_8$	$H_{27}AlSi_3 * C_9$
$H_{24}Be_4O_4 * C_8$	$H_{27}Al_2I_3 * C_{12}$
$H_{24}Ga_4N_4 * C_{12}$	$H_{27}B * C_{12}$
$H_{24}GeO * C_{22}$	$H_{27}B * C_{12}$
$H_{24}In_2N_2 * C_8$	$H_{27}B * C_{12}$
$H_{24}LiSn_2Ti * C_8$	$H_{27}B * C_{15}$
$H_{24}N_3P_2Si * C_8$	$H_{27}B * C_{16}$
$H_{24}O_4Si_4 * C_8$	$H_{27}B * C_{24}$
$H_{24}Si_2 * C_{21}$	$H_{27}BN_2Si * C_{22}$
$H_{24}Sr * C_{28}$	$H_{27}BO_3 * C_{12}$
$H_{25}Al * C_{20}$	$H_{27}BSi * C_{13}$
$H_{25}Al * C_{31}$	$H_{27}B_2O_6 * C_{12}$
$H_{25}Al * C_{32}$	$H_{27}BeBrN_2 * C_{11}$
$H_{25}AlO * C_{22}$	$H_{27}Be_3N_3 * C_9$
$H_{25}AlO * C_{28}$	$H_{27}Br_3In_2 * C_{12}$
$H_{25}AlSi * C_{22}$	$H_{27}ClMgSn * C_{12}$
$H_{25}B * C_{13}$	$H_{27}Fe_3Ti * C_{30}$
$H_{25}B * C_{15}$	$H_{27}Ga * C_{12}$

- $H_{27}Ga^*C_{18}$
 $H_{27}Ga^*C_{24}$
 $H_{27}GaN_2^*C_{11}$
 $H_{27}GaSi_3^*C_9$
 $H_{27}I_3In_2^*C_{12}$
 $H_{27}In^*C_{12}$
 $H_{27}In^*C_{24}$
 $H_{27}InSi_3^*C_9$
 $H_{27}LiSi_3^*C_{10}$
 $H_{27}LiSn^*C_{12}$
 $H_{27}NSi_3^*C_9$
 $H_{27}PSi_3^*C_9$
 $H_{27}Si_3Ti^*C_9$
 $H_{27}Si_3Ti^*C_9$
 $H_{27}Ti^*C_{12}$
 $H_{28}AlLi^*C_{12}$
 $H_{28}AlNa^*C_{12}$
 $H_{28}BLiO_2^*C_{20}$
 $H_{28}BNSn_2^*C_{10}$
 $H_{28}B_2^*C_{12}$
 $H_{28}B_2^*C_{13}$
 $H_{28}B_4^*C_{16}$
 $H_{28}B_{10}O_2^*C_{14}$
 $H_{28}B_{10}S^*C_8$
 $H_{28}BeO^*C_{12}$
 $H_{28}Be_2^*C_{12}$
 $H_{28}GaLi^*C_{12}$
 $H_{28}Ga_4O_4^*C_8$
 $H_{28}MgN_2^*C_{18}$
 $H_{28}Sn^*C_{12}$
 $H_{28}Sn^*C_{22}$
 $H_{29}Al^*C_{14}$
 $H_{29}Al^*C_{14}$
 $H_{29}AlN_2^*C_{12}$
 $H_{29}B^*C_{16}$
 $H_{29}BN_2Sn^*C_{11}$
 $H_{29}BSi^*C_{24}$
 $H_{29}BrMgOSi^*C_{14}$
 $H_{29}LiOSi^*C_{14}$
 $H_{30}AlN^*C_{12}$
 $H_{30}Al_2^*C_{12}$
 $H_{30}Al_2Na_2^*C_{14}$
 $H_{30}Al_3Cl_6Ga^*C_{12}$
 $H_{30}Al_6^*C_{14}$
 $H_{30}BGeLi^*C_{36}$
 $H_{30}BLiSi^*C_{36}$
 $H_{30}BNSi^*C_{24}$
 $H_{30}B_2^*C_{12}$
 $H_{30}B_2^*C_{15}$
 $H_{30}B_2^*C_{16}$
 $H_{30}B_2^*C_{16}$
 $H_{30}B_2^*C_{18}$
 $H_{30}B_2N_2Sn_2^*C_{10}$
 $H_{30}B_2O^*C_{13}$
 $H_{30}Ba^*C_{38}$
 $H_{30}BaGe_2^*C_{36}$
 $H_{30}BaSi_2^*C_{36}$
 $H_{30}BeN_2^*C_{12}$
 $H_{30}BeO_2^*C_{12}$
 $H_{30}BeO_2^*C_{16}$
 $H_{30}Be_2N_2^*C_{14}$
 $H_{30}Be_2N_2^*C_{18}$
 $H_{30}BrGaGe_2^*C_{12}$
 $H_{30}BrMgNSn^*C_{24}$
 $H_{30}Br_2Mg_2Sn_2^*C_{36}$
 $H_{30}CaO_2^*C_{22}$
 $H_{30}CaO_2^*C_{26}$
 $H_{30}CaO_2^*C_{28}$
 $H_{30}CaSi_2^*C_{36}$
 $H_{30}ClIrOP_2^*C_{37}$
 $H_{30}Cl_2NiP_2^*C_{36}$
 $H_{30}Ga_2N_2^*C_{11}$
 $H_{30}Ge_2^*C_{34}$
 $H_{30}Ge_2^*C_{36}$
 $H_{30}Ge_2Mg^*C_{36}$
 $H_{30}Ge_2Sr^*C_{36}$
 $H_{30}LiSn_3Ti^*C_{10}$
 $H_{30}Mg^*C_{16}$
 $H_{30}Mg^*C_{38}$
 $H_{30}MgSn_2^*C_{36}$
 $H_{30}MgSn_2^*C_{36}$
 $H_{30}Pb_2^*C_{36}$
 $H_{30}Si_2^*C_{36}$
 $H_{30}Si_2^*C_{36}$
 $H_{30}Si_2^*C_{36}$
 $H_{30}Si_2Sr^*C_{36}$
 $H_{30}Sn_2^*C_{12}$
 $H_{30}Sn_2^*C_{36}$
 $H_{31}Al^*C_{15}$
 $H_{31}AlO^*C_{13}$
 $H_{31}B^*C_{16}$
 $H_{31}BSi_2^*C_{12}$
 $H_{31}BeN^*C_{13}$
 $H_{31}BeN^*C_{13}$
 $H_{31}CaClO_2^*C_{27}$
 $H_{31}Ga^*C_{14}$
 $H_{31}Ga^*C_{14}$
 $H_{32}Al_2Ba^*C_{12}$
 $H_{32}BLiSi_2^*C_{14}$
 $H_{32}B_2BeO_2F_4^*C_{10}$
 $H_{32}B_{10}Br_{10}N_2^*C_{12}$
 $H_{32}B_{10}S_2^*C_8$
 $H_{32}Be_2^*C_{22}$
 $H_{32}In_2P_2^*C_{12}$

$H_{32}Li^*C_{16}$	$H_{37}AlSn^*C_{16}$
$H_{33}Al^*C_{15}$	$H_{37}B^*C_{18}$
$H_{33}Al^*C_{21}$	$H_{38}AlClSi_4^*C_{14}$
$H_{33}AlSi_3^*C_{12}$	$H_{38}B_1^*C_{16}$
$H_{33}B^*C_{15}$	$H_{38}B_2N_2^*C_{16}$
$H_{33}B^*C_{18}$	$H_{38}B_2Si^*C_{18}$
$H_{33}B^*C_{21}$	$H_{38}Ba^*C_{42}$
$H_{33}BN_2O_3Si^*C_{13}$	$H_{38}BaGe_2O^*C_{40}$
$H_{33}BSi_3^*C_{12}$	$H_{38}Be_2K_2O_2^*C_{16}$
$H_{33}B_3O_6^*C_{18}$	$H_{38}CaO^*C_{42}$
$H_{33}B_{18}N^*C_7$	$H_{38}Ge_2MgO_4^*C_{14}$
$H_{33}ClMgPb^*C_{15}$	$H_{38}Ge_2OSr^*C_{40}$
$H_{33}ClMgPbSi_3^*C_{12}$	$H_{39}Al^*C_{18}$
$H_{33}Ga^*C_{15}$	$H_{39}Al^*C_{18}$
$H_{33}Ga^*C_{18}$	$H_{39}AlSi_3^*C_{15}$
$H_{33}Ga^*C_{27}$	$H_{39}Ga^*C_{30}$
$H_{33}GaSi_3^*C_{12}$	$H_{39}In^*C_{30}$
$H_{33}In^*C_{18}$	$H_{40}AlGaLi_2^*C_{16}$
$H_{33}InSi_3^*C_{12}$	$H_{40}AlLi^*C_{56}$
$H_{33}InSi_3^*C_{12}$	$H_{40}AlSb^*C_{16}$
$H_{34}CaO_2^*C_{34}$	$H_{40}Al_2Ba^*C_{16}$
$H_{34}GeSi_3^*C_{12}$	$H_{40}Al_2Ca^*C_{16}$
$H_{34}MgN_2Si_2^*C_{12}$	$H_{40}Al_2Ca^*C_{16}$
$H_{34}MgO_2Si_2^*C_{14}$	$H_{40}Al_2Sr^*C_{16}$
$H_{34}Si_3Sn^*C_{12}$	$H_{40}B_4Sn^*C_{48}$
$H_{35}AlGe_3O^*C_{13}$	$H_{40}Be_4S_4^*C_{16}$
$H_{35}AlO^*C_{38}$	$H_{40}Li_2Si_4^*C_{48}$
$H_{35}AlOSi_3^*C_{13}$	$H_{42}AlLiSn^*C_{18}$
$H_{35}AlOSi_3^*C_{13}$	$H_{42}Al_2N_2P_2Si^*C_{14}$
$H_{35}AlOSn_3^*C_{13}$	$H_{42}BNSi^*C_{40}$
$H_{35}AlSi_2^*C_{38}$	$H_{42}B_2N_2^*C_{16}$
$H_{35}B^*C_{20}$	$H_{42}B_2N_2^*C_{18}$
$H_{35}BO^*C_{18}$	$H_{42}B_2N_2^*C_{20}$
$H_{35}GaOSi_3^*C_{13}$	$H_{42}Be_2N_2^*C_{16}$
$H_{36}AlKS_4^*C_{12}$	$H_{42}Be_2N_2^*C_{20}$
$H_{36}AlLiSi_4^*C_{12}$	$H_{42}Ga_2N_2^*C_{17}$
$H_{36}AlLiSn^*C_{15}$	$H_{42}Sn_2^*C_{18}$
$H_{36}AlNa^*C_{24}$	$H_{43}AlO^*C_{19}$
$H_{36}AlNaSi_4^*C_{12}$	$H_{44}GaK^*C_{28}$
$H_{36}AlNaSi_4^*C_{12}$	$H_{45}Al^*C_{21}$
$H_{36}BLiSi_4^*C_{12}$	$H_{45}AlClKS_3^*C_{54}$
$H_{36}B_2BeP_4^*C_{12}$	$H_{45}AlSi_3^*C_{54}$
$H_{36}B_2Si^*C_{15}$	$H_{45}GaGe_3^*C_{18}$
$H_{36}Be_3^*C_{15}$	$H_{45}Ge_3In^*C_{18}$
$H_{36}GaK^*C_{24}$	$H_{45}Ge_3Tl^*C_{18}$
$H_{36}GaLi^*C_{16}$	$H_{45}Ge_3Tl^*C_{18}$
$H_{36}GaPSi^*C_{26}$	$H_{45}Si_3Tl^*C_{18}$
$H_{36}LiSn_4Tl^*C_{12}$	$H_{45}Sn_3Tl^*C_{18}$
$H_{36}MgN_2Si_2^*C_{13}$	$H_{46}BNSi_4^*C_{50}$
$H_{36}O_4Ti^*C_{16}$	$H_{46}B_2^*C_{20}$
$H_{37}AlO^*C_{16}$	$H_{46}B_2N_2^*C_{20}$
$H_{37}AlOSi_3^*C_{13}$	$H_{46}Be_2Li_2O_4^*C_{20}$

H ₄₇ B*C ₂₄	Catalyst for the reaction of R ₃ SiCl with
H ₄₈ AlClOSi ₄ *C ₁₈	Al metal: 5.3.8.4
H ₄₈ B ₂ Br ₄ CoP ₄ *C ₅₂	Hg*Br ₂
H ₄₈ Be ₄ O ₄ *C ₂₀	Hg*C ₂ H ₂ Cl ₂
H ₅₀ Al ₂ N ₂ *C ₂₂	Hg*C ₂ H ₆
H ₅₁ Al*C ₂₄	Hg*C ₂ H ₆
H ₅₁ Al ₂ I ₃ *C ₂₄	Hg*C ₂ H ₆
H ₅₁ B*C ₃₀	Hg*C ₄ H ₆
H ₅₂ AlLi*C ₃₂	Hg*C ₄ H ₆
H ₅₂ AlNaSi ₄ *C ₂₆	Hg*C ₄ H ₁₀
H ₅₂ GaK*C ₃₂	Hg*C ₄ H ₁₀
H ₅₂ GaNa*C ₂₄	Hg*C ₄ H ₂₂ B ₂₀
H ₅₄ AlPSj ₆ *C ₁₈	Hg*C ₆ H ₆
H ₅₄ Al ₂ *C ₂₄	Hg*C ₆ H ₁₀
H ₅₄ Al ₂ Na ₂ *C ₂₆	Hg*C ₆ H ₁₀
H ₅₄ B ₂ N ₂ *C ₂₆	Hg*C ₆ H ₁₄
H ₅₄ Be ₂ N ₂ *C ₃₀	Hg*C ₆ H ₁₈ Ge ₂
H ₅₄ Be ₃ O ₆ *C ₂₄	Hg*C ₈ H ₄ Ba
H ₅₄ Sn ₂ *C ₂₄	Hg*C ₈ H ₁₄
H ₅₅ Al ₂ Sb*C ₂₂	Hg*C ₈ H ₁₈
H ₅₆ GaK*C ₄₈	Hg*C ₁₀ H ₁₀
H ₅₇ Al*C ₂₇	Hg*C ₁₀ H ₂₂
H ₅₇ GaSi ₆ *C ₂₁	Hg*C ₁₂ H ₁₀
H ₅₇ In*C ₂₇	Hg*C ₁₂ H ₁₀
H ₅₇ InSi ₆ *C ₂₁	Hg*C ₁₂ H ₁₀
H ₆₀ Al ₂ *C ₉₄	Hg*C ₁₄ H ₁₄
H ₆₀ B ₃ N ₃ Si ₃ *C ₇₂	Hg*C ₁₆ H ₁₀
H ₆₀ GaNa*C ₂₈	Hg*C ₂₀ H ₁₄
H ₆₀ NiP ₄ *C ₇₂	Hg*C ₃₂ H ₂₀ Ba
H ₆₃ Al*C ₃₀	Hg*Cl ₂
H ₆₃ Ga*C ₃₀	Hg*Cl ₂
H ₆₃ In*C ₃₀	Hg*Cl ₂
H ₆₃ In*C ₃₉	Hg*H ₂
H ₆₆ AlKO ₃ Si ₄ *C ₂₄	HgK ₂ N ₄ *C ₄
H ₆₆ AlLiO ₃ Si ₄ *C ₂₄	HgSi ₂ *C ₆ H ₁₈
H ₆₆ GaLiO ₃ Si ₄ *C ₂₄	HgSi ₂ *C ₆ H ₁₈
H ₆₈ B ₂ CoP ₄ *C ₇₆	HgSi ₂ *C ₆ H ₁₈
H ₆₈ GaNa*C ₃₂	HgSi ₂ *C ₈ H ₂₂
H ₆₉ Al*C ₃₃	HgSi ₂ *C ₁₆ H ₂₂
H ₆₉ B*C ₃₆	HgSn ₂ *C ₆ H ₁₈
H ₇₀ Al ₂ N ₂ Si ₆ *C ₂₄	HgTl
H ₇₄ Al ₄ O ₄ *C ₄₀	Tl-Hg
H ₇₅ Al*C ₃₆	Reaction with C ₅ Cl ₆ : 5.3.6.2.1
H ₇₈ AlLiO ₄ Si ₄ *C ₂₈	Hg ₂ *C ₃ H ₆ Br ₂
H ₈₁ BBr ₂ P ₆ Sn*C ₈₁	Hg ₂ *C ₅ H ₁₂
H ₉₉ B ₂ Br ₂ P ₈ Sn*C ₁₀₅	I*CH ₃ Ca
H ₉₉ Ge ₃ Si ₉ Tl*C ₃₆	I*CH ₃ Ca
H ₉₉ Si ₉ Sn ₃ Tl*C ₃₆	I*CH ₃ Ca
H ₁₁₆ AlNaO ₈ Si ₄ *C ₄₄	I*C ₂ H ₅ Ca
Hg	I*C ₂ H ₆ B
Hg	I*C ₃ H ₇ Ca
Catalyst for the formation of LiGa(Si*Me ₃) ₄ : 5.3.9	I*C ₄ H ₉ Ca

$I^*C_4H_{10}Al$ $I^*C_4H_{10}B$ $I^*C_4H_{10}Ga$ $I^*C_5H_5Be$ $I^*C_5H_{12}Al$ $I^*C_5H_{12}Ga$ $I^*C_6CaF_5$ $I^*C_6F_5$ $I^*C_6H_5$ $I^*C_6H_5Ca$ $I^*C_7H_7$ $I^*C_7H_{15}Ca$ $I^*C_8H_5Ca$ $I^*C_9H_7Ca$ $I^*C_{10}H_7Ca$ $I^*C_{10}H_9Fe$ $I^*C_{10}H_{18}B$ $I^*C_{11}H_{12}BFe$ $I^*C_{12}H_{10}B$ $I^*C_{12}H_{10}BF_4$ $I^*C_{12}H_{10}Ga$ $I^*C_{12}H_{26}B$ $I^*C_{13}H_9Ca$ $I^*C_{15}H_{15}Ca$ $I^*C_{16}H_{14}BFe$ $I^*C_{19}H_{15}Ca$ I^*Cu **In****InI**

Formation: 5.3.5.2.1, 5.3.5.2.2

Reaction with RI: 5.3.5.3.3

 $In^*C_2H_6$ $In^*C_4H_{10}$ $In^*C_{10}H_{10}$ $In^*C_{12}F_{10}$ $In^*C_{12}H_{10}$ $In^*C_{14}H_{14}$ $InN_2^*C_6H_8$ $In_2^*CH_2Cl_3$ **IK****KI**

Complexing agent for isobutylaluminum: 5.3.5.3.1

 $IMg^*B_{10}H_{13}$ $IMg^*B_{10}H_{13}$ IMg^*CD_3 IMg^*CH_3 $IMg^*C_4H_9$ $IMg^*C_{19}H_{13}$ $IMg^*C_{19}H_{15}$ $IMg^*C_{20}H_{13}$ $IMgN^*C_8H_{10}$ $IMnO_3^*C_9H_7B$ $IMnO_3^*C_{10}H_9B$ $IMnO_3^*C_{14}H_9B$ $IMnO_3^*C_{15}H_{11}B$ $IN^*C_3H_4$ $IN_2^*C_{12}H_{17}Ca$ $IN_2Ti^*C_6H_8$ $IO^*C_6H_{13}Ba$ $IO^*C_7H_7Ca$ $IO_2^*C_{10}H_{13}Ca$ $IO_2^*C_{11}H_{15}Ca$ $IO_2^*C_{13}H_{21}Ca$ $IO_2Sr^*C_9H_{19}$ $IO_2Sr^*C_{10}H_{21}$ $IO_2Sr^*C_{11}H_{23}$ $IO_2Sr^*C_{12}H_{25}$ $IS^*C_2H_8B$ $ISSr^*C_4H_3$ $ISr^*C_6H_5$ $ISr^*C_7H_7$ $ISr^*C_{10}H_7$ **ITl****TII**

Reaction with RLi and RI: 5.3.6.3.2

 $ITl^*C_2H_6$ $ITl^*C_4H_{10}$ **I₂****I₂**

Catalyst in RMgX formation: 5.4.2.2.1

Catalyst in the reaction of In metal

with HgR_2 : 5.3.5.2.5

Reaction with Ga metal and RX:

5.3.4.2.1

 $I_2^*CH_3B$ $I_2^*C_2H_5B$ $I_2^*C_4H_9B$ $I_2^*C_6H_4$ $I_2^*C_6H_5B$ $I_2^*C_6H_5B$ $I_2^*C_6H_5Ga$ $I_2^*C_{10}H_9BFe$ $I_2^*C_{12}H_8B_2$ I_2^*Ge $I_2In^*CH_3$ $I_2In^*CH_3$ $I_2In^*C_2H_5$ $I_2In^*C_3H_7$ $I_2In^*C_4H_9$ $I_2In^*C_5H_5$ $I_2In^*C_6F_5$ $I_2In^*C_6H_5$ $I_2K_2Mg^*C_{16}$

I_2Mg	In^*Br_2
MgI_2	In^*Br_3
Formation: 5.4.2.3.1	In^*CH_3
Reaction with RLi: 5.4.2.3.1	$In^*CH_3Br_2$
Reaction with RNa: 5.4.2.3.1	$In^*CH_3Cl_2$
Reaction with radicals: 5.4.2.3.3	$In^*CH_3I_2$
Redistribution with MgR_2 : 5.4.2.3.2	$In^*CH_3I_2$
$I_2Mg_2*CH_2$	$In^*C_2H_5$
$I_2MnO_3*C_8H_4B$	$In^*C_2H_5Br_2$
$I_2MnO_3*C_9H_6B$	$In^*C_2H_5I_2$
$I_2S*C_2H_7B$	$In^*C_2H_6Br$
$I_2S*C_6H_{10}B_2$	$In^*C_2H_6Cl$
I_3*Al	$In^*C_2H_6I$
I_3*B	$In^*C_3H_7Br_2$
I_3*B	$In^*C_3H_7I_2$
I_3*B	$In^*C_3H_9$
I_3*B	$In^*C_3H_9$
$I_3*C_3H_9Al_2$	$In^*C_3H_9$
$I_3*C_3H_9Ga_2$	$In^*C_3H_9$
$I_3*C_6H_{10}B$	$In^*C_4H_9Br_2$
$I_3*C_6H_{15}Al_2$	$In^*C_4H_9I_2$
$I_3*C_6H_{15}Ga_2$	$In^*C_4H_{10}Cl$
$I_3*C_8H_6B$	$In^*C_4H_{10}I$
$I_3*C_{12}H_{27}Al_2$	$In^*C_5H_5$
$I_3*C_{18}H_{15}Al_2$	$In^*C_5H_5I_2$
$I_3*C_{24}H_{51}Al_2$	$In^*C_6Cl_2F_5$
I_3*Ga	$In^*C_6F_5I_2$
$I_3In_2*C_3H_9$	$In^*C_6H_4Br_2F$
$I_3In_2*C_3H_9$	$In^*C_6H_5Br_2$
$I_3In_2*C_6H_{15}$	$In^*C_6H_5Cl_2$
$I_3In_2*C_9H_{21}$	$In^*C_6H_5Cl_2$
$I_3In_2*C_{12}H_{27}$	$In^*C_6H_5I_2$
$I_3S_3*B_3$	$In^*C_6H_{15}$
I_4*C	$In^*C_6H_{15}$
$I_4*C_2H_6Ga_2$	$In^*C_7H_7Br_2$
$I_4*C_4H_{10}Ga_2$	$In^*C_7H_{11}$
$I_4*C_6H_{14}Ga_2$	$In^*C_6H_{15}$
$I_4*C_9H_{18}Ga_2$	$In^*C_9H_{21}$
$I_4*C_{10}H_8B_2Fe$	$In^*C_9H_{21}$
$I_4MnO_3*C_8H_3B_2$	$In^*C_{10}H_{10}I$
$I_5In_2*CH_3$	$In^*C_{12}BrF_{10}$
In	$In^*C_{12}ClF_{10}$
In	$In^*C_{12}F_{10}I$
Formation from $InCl_3$: 5.3.5.2.2	$In^*C_{12}H_8BrF_2$
Reaction with CpH: 5.3.5.2.4	$In^*C_{12}H_{10}Br$
Reaction with EtI: 5.3.5.2.2	$In^*C_{12}H_{10}Cl$
Reaction with HgR_2 : 5.3.5.2.5	$In^*C_{12}H_{10}I$
Reaction with RI: 5.3.5.2.2	$In^*C_{12}H_{27}$
Reaction with RX: 5.3.5.2.1	$In^*C_{14}H_{14}Br$
Reaction with $BrTi(C_6F_5)_2$: 5.3.5.2.6	$In^*C_{14}H_{14}I$
Reaction with C_6H_5I : 5.3.5.2.1	$In^*C_{15}H_{15}$
In^*Br	$In^*C_{18}F_{15}$

$\text{In}^*\text{C}_{18}\text{F}_{15}$
 $\text{In}^*\text{C}_{18}\text{F}_{15}$
 $\text{In}^*\text{C}_{18}\text{H}_{12}\text{Br}_3$
 $\text{In}^*\text{C}_{18}\text{H}_{12}\text{Cl}_3$
 $\text{In}^*\text{C}_{18}\text{H}_{12}\text{F}_3$
 $\text{In}^*\text{C}_{18}\text{H}_{15}$
 $\text{In}^*\text{C}_{18}\text{H}_{15}$
 $\text{In}^*\text{C}_{18}\text{H}_{21}$
 $\text{In}^*\text{C}_{18}\text{H}_{33}$
 $\text{In}^*\text{C}_{18}\text{H}_{45}\text{Ge}_3$
 $\text{In}^*\text{C}_{20}\text{H}_{14}\text{Br}$
 $\text{In}^*\text{C}_{21}\text{H}_{21}$
 $\text{In}^*\text{C}_{24}\text{H}_{27}$
 $\text{In}^*\text{C}_{27}\text{H}_{21}$
 $\text{In}^*\text{C}_{27}\text{H}_{21}\text{Br}$
 $\text{In}^*\text{C}_{27}\text{H}_{57}$
 $\text{In}^*\text{C}_{30}\text{H}_{39}$
 $\text{In}^*\text{C}_{30}\text{H}_{63}$
 $\text{In}^*\text{C}_{39}\text{H}_{63}$
 In^*Cl
 In^*Cl_3
 In^*Cl_3
 In^*I
 $\text{InLiSn}^*\text{C}_6\text{H}_{18}$
InMg
 In–Mg alloy
 Reaction with alkyl bromides: 5.3.5.2.3
 $\text{InN}_2^*\text{C}_6\text{H}_8\text{I}$
 $\text{InN}_2^*\text{C}_8\text{H}_{21}\text{Br}_2$
 $\text{InO}^*\text{C}_7\text{H}_{19}$
 $\text{InO}^*\text{C}_{22}\text{H}_{10}\text{F}_{15}$
 $\text{InO}_2^*\text{C}_2\text{H}_7$
 $\text{InO}_3^*\text{C}_{21}\text{H}_{21}$
 $\text{InO}_4^*\text{C}_8\text{H}_{14}\text{Br}$
 $\text{InP}^*\text{C}_7\text{H}_{20}$
 $\text{InP}^*\text{C}_{36}\text{H}_{15}\text{F}_{15}$
 $\text{InSi}^*\text{C}_4\text{H}_{11}\text{Cl}_2$
 $\text{InSi}_2^*\text{C}_8\text{H}_{22}\text{Cl}$
 $\text{InSi}_3^*\text{C}_9\text{H}_{27}$
 $\text{InSi}_3^*\text{C}_{12}\text{H}_{33}$
 $\text{InSi}_3^*\text{C}_{12}\text{H}_{33}$
 $\text{InSi}_6^*\text{C}_{21}\text{H}_{57}$
 $\text{In}_2^*\text{CH}_2\text{BrCl}_3$
 $\text{In}_2^*\text{CH}_2\text{Cl}_3\text{I}$
 $\text{In}_2^*\text{CH}_2\text{Cl}_4$
 $\text{In}_2^*\text{CH}_3\text{I}_5$
 $\text{In}_2^*\text{C}_3\text{H}_9\text{Br}_3$
 $\text{In}_2^*\text{C}_3\text{H}_9\text{I}_3$
 $\text{In}_2^*\text{C}_3\text{H}_9\text{I}_3$
 $\text{In}_2^*\text{C}_6\text{H}_{15}\text{Br}_3$
 $\text{In}_2^*\text{C}_6\text{H}_{15}\text{I}_3$
 $\text{In}_2^*\text{C}_9\text{H}_{21}\text{Br}_3$

$\text{In}_2^*\text{C}_9\text{H}_{21}\text{I}_3$
 $\text{In}_2^*\text{C}_{12}\text{H}_{27}\text{Br}_3$
 $\text{In}_2^*\text{C}_{12}\text{H}_{27}\text{I}_3$
 $\text{In}_2^*\text{C}_{20}\text{H}_{22}$
 $\text{In}_2\text{N}_2^*\text{C}_8\text{H}_{24}$
 $\text{In}_2\text{P}_2^*\text{C}_{12}\text{H}_{32}$
 $\text{IrOP}_2^*\text{C}_3\text{H}_3\text{OCl}$

K

K

Dehalogenation of R_2AlX , RAlX_2 :

5.3.3.3.4

Reaction with $\text{Hg}(\text{SiR}_3)_2$ and $(\text{R}_3\text{Si})_3^+$

Al^+OEt_2 : 5.3.8.5

Reaction with InCl_3 : 5.3.5.2.2

Reaction with TlCl : 5.3.6.2.1

K^*BF_4
 K^*BF_4
 K^*BGeH_6
 $\text{K}^*\text{C}_4\text{H}_{10}\text{AlCl}_2$
 $\text{K}^*\text{C}_4\text{H}_{12}\text{Ga}$
 K^*C_8
 $\text{K}^*\text{C}_8\text{H}_{18}\text{B}$
 $\text{K}^*\text{C}_8\text{H}_{20}\text{Be}_2\text{F}$
 $\text{K}^*\text{C}_8\text{H}_{20}\text{Ga}$
 $\text{K}^*\text{C}_9\text{H}_9$
 $\text{K}^*\text{C}_{10}\text{H}_{16}\text{Al}$
 $\text{K}^*\text{C}_{13}\text{H}_{11}$
 $\text{K}^*\text{C}_{18}\text{H}_{15}\text{Ge}$
 $\text{K}^*\text{C}_{24}\text{H}_{36}\text{Ga}$
 $\text{K}^*\text{C}_{28}\text{H}_{44}\text{Ga}$
 $\text{K}^*\text{C}_{32}\text{H}_{52}\text{Ga}$
 $\text{K}^*\text{C}_{48}\text{H}_{56}\text{Ga}$
 K^*Cl
 K^*F
 K^*GaH_4
 K^*GeH_3
 K^*I
 KN^*C
 $\text{KN}_2^*\text{C}_4\text{H}_6\text{Ga}$
 $\text{KO}_3^*\text{C}_9\text{H}_{22}\text{B}$
 $\text{KO}_3\text{Si}_4^*\text{C}_{24}\text{H}_{66}\text{Al}$
 $\text{KSi}^*\text{C}_8\text{H}_{21}\text{AlCl}$
 $\text{KSi}^*\text{C}_{18}\text{H}_{15}$
 $\text{KSi}^*\text{C}_{18}\text{H}_{15}$
 KSi^*H_3
 $\text{KSi}_3^*\text{C}_{54}\text{H}_{45}\text{AlCl}$
 $\text{KSi}_4^*\text{C}_{12}\text{H}_{36}\text{Al}$
 $\text{KZn}^*\text{C}_2\text{H}_7$
 KZn_2^*H_5
 $\text{K}_2^*\text{C}_6\text{H}_{18}\text{Ga}_2$
 $\text{K}_2^*\text{C}_8\text{H}_8$
 $\text{K}_2^*\text{C}_8\text{H}_8$

$K_2Mg \cdot C_{16}I_2$
 $K_2N_4 \cdot C_4Hg$
 $K_2O_2 \cdot C_{16}H_{38}Be_2$
 $K_2Si \cdot F_6$

Li**Li**

Reaction with Al metal and R_3SiCl :

5.3.8.4

Reaction with GaX_3 and R_3SiX : 5.3.9

Reaction with Ga metal and R_3SiCl :

5.3.9

Reaction with PbR_4 : 5.4.7.2.3

Reaction with R_3SiX and Li metal:

5.3.10

$Li \cdot AlH_4$
 $Li \cdot AlH_4$
 $Li \cdot AlH_4$
 $Li \cdot AlH_4$
 $Li \cdot AlH_4$
 $Li \cdot B_5H_8$
 $Li \cdot CH_3$
 $Li \cdot C_2H_9B_8$
 $Li \cdot C_3H_3$
 $Li \cdot C_3H_9Be$
 $Li \cdot C_3H_9Ge$
 $Li \cdot C_3H_{14}B_9$
 $Li \cdot C_4H_9$
 $Li \cdot C_4H_{12}Ga$
 $Li \cdot C_4H_{20}B_{17}$
 $Li \cdot C_5H_5$
 $Li \cdot C_5H_{15}Be_2$
 $Li \cdot C_6F_5$
 $Li \cdot C_6H_5$
 $Li \cdot C_6H_5B$
 $Li \cdot C_8H_5$
 $Li \cdot C_8H_5B_2Co$
 $Li \cdot C_8H_{11}$
 $Li \cdot C_8H_{12}Al$
 $Li \cdot C_8H_{12}Al$
 $Li \cdot C_8H_{14}AlGe$
 $Li \cdot C_8H_{15}$
 $Li \cdot C_8H_{16}$
 $Li \cdot C_8H_{20}Ga$
 $Li \cdot C_9H_{19}B$
 $Li \cdot C_{12}H_{12}Al$
 $Li \cdot C_{12}H_{28}Al$
 $Li \cdot C_{12}H_{28}Ga$
 $Li \cdot C_{13}H_{16}AlGe$
 $Li \cdot C_{16}H_{15}$
 $Li \cdot C_{16}H_{32}$
 $Li \cdot C_{16}H_{36}Ga$
 $Li \cdot C_{18}H_{15}Be$

$Li \cdot C_{18}H_{15}Ge$
 $Li \cdot C_{18}H_{18}AlGe$
 $Li \cdot C_{20}H_{13}$
 $Li \cdot C_{21}H_{21}Be$
 $Li \cdot C_{24}H_{20}Al$
 $Li \cdot C_{32}H_{20}Al$
 $Li \cdot C_{32}H_{52}Al$
 $Li \cdot C_{36}H_{30}BGe$
 $Li \cdot C_{56}H_{40}Al$
 $Li \cdot H$
 $LiMg \cdot CH_5$
 $LiMg_2 \cdot C_8H_{21}$
 $LiMg_2 \cdot H_5$
 $LiN \cdot C_6H_{15}Be$
 $LiN \cdot C_8H_{10}$
 $LiN \cdot C_9H_{18}$
 $LiOSi \cdot C_{14}H_{29}$
 $LiO_2 \cdot C_{20}H_{28}B$
 $LiO_2S \cdot C_9H_9$
 $LiO_2S \cdot C_{14}H_{11}$
 $LiO_3Si_4 \cdot C_{24}H_{66}Al$
 $LiO_3Si_4 \cdot C_{24}H_{66}Ga$
 $LiO_4Si_4 \cdot C_{28}H_{78}Al$
 $LiP \cdot C_4H_{10}$
 $LiPb \cdot C_3H_9$
 $LiS \cdot C_4H_3$
 $LiSi \cdot C_3H_9$
 $LiSi \cdot C_8H_{11}$
 $LiSi \cdot C_{11}H_{20}Al$
 $LiSi \cdot C_{18}H_{15}$
 $LiSi \cdot C_{18}H_{15}$
 $LiSi \cdot C_{18}H_{15}$
 $LiSi \cdot C_{18}H_{18}Al$
 $LiSi \cdot C_{36}H_{30}B$
 $LiSi_2 \cdot C_7H_{19}$
 $LiSi_2 \cdot C_{14}H_{32}B$
 $LiSi_3 \cdot C_{10}H_{27}$
 $LiSi_4 \cdot C_{12}H_{36}Al$
 $LiSi_4 \cdot C_{12}H_{36}B$
 $LiSn \cdot C_3H_9$
 $LiSn \cdot C_3H_9$
 $LiSn \cdot C_3H_{12}B$
 $LiSn \cdot C_6H_{15}$
 $LiSn \cdot C_6H_{18}Al$
 $LiSn \cdot C_6H_{18}Ga$
 $LiSn \cdot C_6H_{18}In$
 $LiSn \cdot C_{12}H_{27}$
 $LiSn \cdot C_{15}H_{36}Al$
 $LiSn \cdot C_{18}H_{42}Al$
 $LiSnTl \cdot C_6H_{18}$
 $LiSn_2Tl \cdot C_8H_{24}$
 $LiSn_3Tl \cdot C_{10}H_{30}$

$\text{LiSn}_4\text{Ti}^*\text{C}_{12}\text{H}_{36}$	$\text{Mg}^*\text{C}_2\text{H}_5\text{Br}$
$\text{LiTi}^*\text{C}_4\text{H}_{12}$	$\text{Mg}^*\text{C}_2\text{H}_5\text{Cl}$
$\text{LiZn}^*\text{C}_2\text{H}_7$	$\text{Mg}^*\text{C}_2\text{H}_6$
$\text{LiZn}^*\text{C}_2\text{H}_{10}\text{Al}$	$\text{Mg}^*\text{C}_2\text{H}_6$
$\text{Li}_2^*\text{C}_4\text{H}_{12}\text{Be}$	$\text{Mg}^*\text{C}_2\text{H}_6$
$\text{Li}_2^*\text{C}_6\text{H}_4$	$\text{Mg}^*\text{C}_2\text{H}_8\text{Li}_2$
$\text{Li}_2^*\text{C}_{10}\text{H}_{25}\text{Ga}$	$\text{Mg}^*\text{C}_3\text{H}_3\text{Br}$
$\text{Li}_2^*\text{C}_{16}\text{H}_{40}\text{AlGa}$	$\text{Mg}^*\text{C}_3\text{H}_5\text{Br}$
$\text{Li}_2^*\text{C}_{28}\text{H}_{20}$	$\text{Mg}^*\text{C}_3\text{H}_5\text{Br}$
$\text{Li}_2^*\text{C}_{32}\text{H}_{20}\text{Be}$	$\text{Mg}^*\text{C}_3\text{H}_5\text{Cl}$
$\text{Li}_2\text{Mg}^*\text{C}_2\text{H}_8$	$\text{Mg}^*\text{C}_3\text{H}_7\text{Br}$
$\text{Li}_2\text{O}_4^*\text{C}_{20}\text{H}_{46}\text{Be}_2$	$\text{Mg}^*\text{C}_3\text{H}_7\text{Cl}$
$\text{Li}_2\text{S}^*\text{C}_3\text{H}_4$	$\text{Mg}^*\text{C}_3\text{H}_8$
$\text{Li}_2\text{S}^*\text{C}_4\text{H}_6$	$\text{Mg}^*\text{C}_4\text{H}_6$
$\text{Li}_2\text{Si}_4^*\text{C}_{48}\text{H}_{40}$	$\text{Mg}^*\text{C}_4\text{H}_7\text{Cl}$
$\text{Li}_2\text{Zn}^*\text{C}_4\text{H}_{12}$	$\text{Mg}^*\text{C}_4\text{H}_7\text{Cl}_2$
$\text{Li}_3^*\text{C}_5\text{H}_{15}\text{Be}$	$\text{Mg}^*\text{C}_4\text{H}_8$
Mg	$\text{Mg}^*\text{C}_4\text{H}_9\text{Br}$
Mg	$\text{Mg}^*\text{C}_4\text{H}_9\text{Br}$
Alloy with Al metal: 5.3.3.2.2	$\text{Mg}^*\text{C}_4\text{H}_9\text{Cl}$
Formation of activated Mg: 5.4.2.2.1	$\text{Mg}^*\text{C}_4\text{H}_9\text{Cl}$
Reaction with B_2O_3 : 5.3.2.1.1	$\text{Mg}^*\text{C}_4\text{H}_9\text{Cl}$
Reaction with $\text{Hg}(\text{GeR}_3)_2$: 5.4.5.5	$\text{Mg}^*\text{C}_4\text{H}_9\text{Cl}$
Reaction with $\text{Hg}(\text{SiMe}_2\text{Ph})_2$: 5.4.4.4	$\text{Mg}^*\text{C}_4\text{H}_9\text{I}$
Reaction with $\text{Hg}(\text{SiR}_3)_2$: 5.4.4.4	$\text{Mg}^*\text{C}_4\text{H}_{10}$
Reaction with Ph_3SnCl : 5.4.6.2	$\text{Mg}^*\text{C}_4\text{H}_{10}$
Reaction with Ph_6Sn_2 : 5.4.6.3	$\text{Mg}^*\text{C}_4\text{H}_{10}$
Reaction with R_3PbX : 5.4.7.2.4	$\text{Mg}^*\text{C}_4\text{H}_{10}$
Reaction with Sn metal: 5.4.6.1	$\text{Mg}^*\text{C}_4\text{H}_{10}$
Reaction with R_3GeCl : 5.4.5.2	$\text{Mg}^*\text{C}_5\text{H}_5\text{Br}$
Reaction with olefins: 5.4.2.2.4	$\text{Mg}^*\text{C}_5\text{H}_6$
Mg^*B_2	$\text{Mg}^*\text{C}_5\text{H}_7\text{Br}$
$\text{Mg}^*\text{B}_{10}\text{H}_{13}\text{I}$	$\text{Mg}^*\text{C}_5\text{H}_9\text{Cl}$
$\text{Mg}^*\text{B}_{10}\text{H}_{13}\text{I}$	$\text{Mg}^*\text{C}_5\text{H}_{10}$
Mg^*BrH	$\text{Mg}^*\text{C}_5\text{H}_{11}\text{Br}$
Mg^*BrH	$\text{Mg}^*\text{C}_5\text{H}_{11}\text{Cl}$
Mg^*Br_2	$\text{Mg}^*\text{C}_5\text{H}_{11}\text{Cl}$
Mg^*Br_2	$\text{Mg}^*\text{C}_5\text{H}_{12}$
Mg^*Br_2	$\text{Mg}^*\text{C}_5\text{H}_{15}\text{Al}$
Mg^*CCl_4	$\text{Mg}^*\text{C}_6\text{BrF}_5$
$\text{Mg}^*\text{CD}_3\text{I}$	$\text{Mg}^*\text{C}_6\text{H}_5\text{Br}$
$\text{Mg}^*\text{CH}_3\text{Br}$	$\text{Mg}^*\text{C}_6\text{H}_5\text{Br}$
$\text{Mg}^*\text{CH}_3\text{Br}$	$\text{Mg}^*\text{C}_6\text{H}_5\text{Cl}$
$\text{Mg}^*\text{CH}_3\text{Br}$	$\text{Mg}^*\text{C}_6\text{H}_6$
$\text{Mg}^*\text{CH}_3\text{Br}$	$\text{Mg}^*\text{C}_6\text{H}_6$
$\text{Mg}^*\text{CH}_3\text{Cl}$	$\text{Mg}^*\text{C}_6\text{H}_6$
$\text{Mg}^*\text{CH}_3\text{I}$	$\text{Mg}^*\text{C}_6\text{H}_9\text{Br}$
Mg^*CH_4	$\text{Mg}^*\text{C}_6\text{H}_{11}\text{Br}$
$\text{Mg}^*\text{CH}_5\text{Li}$	$\text{Mg}^*\text{C}_6\text{H}_{11}\text{Cl}$
$\text{Mg}^*\text{C}_2\text{HBr}$	$\text{Mg}^*\text{C}_6\text{H}_{12}$
$\text{Mg}^*\text{C}_2\text{H}_3\text{Br}$	$\text{Mg}^*\text{C}_6\text{H}_{13}\text{F}$
$\text{Mg}^*\text{C}_2\text{H}_5\text{Br}$	$\text{Mg}^*\text{C}_6\text{H}_{14}$

Mg*C ₆ H ₁₄	Mg*C ₁₈ H ₁₅ BrGe
Mg*C ₆ H ₁₄	Mg*C ₁₈ H ₁₅ BrGe
Mg*C ₇ H ₇ Br	Mg*C ₁₈ H ₁₅ ClGe
Mg*C ₇ H ₇ Cl	Mg*C ₁₈ H ₂₂
Mg*C ₇ H ₉ Cl	Mg*C ₁₉ H ₁₃ Br
Mg*C ₇ H ₁₁ Cl	Mg*C ₁₉ H ₁₃ I
Mg*C ₇ H ₁₃ Cl	Mg*C ₁₉ H ₁₅ Br
Mg*C ₈ H ₇ Br	Mg*C ₁₉ H ₁₅ Br
Mg*C ₈ H ₇ Cl	Mg*C ₁₉ H ₁₅ I
Mg*C ₈ H ₈	Mg*C ₁₉ H ₂₅
Mg*C ₈ H ₉ Br	Mg*C ₂₀ H ₁₃ I
Mg*C ₈ H ₁₂	Mg*C ₂₀ H ₂₆
Mg*C ₈ H ₁₈	Mg*C ₃₆ H ₃₀ Ge ₂
Mg*C ₈ H ₁₈	Mg*C ₃₈ H ₃₀
Mg*C ₈ H ₁₈	Mg*ClH
Mg*C ₈ H ₁₈	Mg*Cl ₂
Mg*C ₈ H ₂₄ Al ₂	Mg*F ₂
Mg*C ₉ H ₇ Br	Mg*Ga
Mg*C ₉ H ₇ Cl	Mg*H ₂
Mg*C ₉ H ₉ Br	Mg*H ₂
Mg*C ₉ H ₁₁ Br	Mg*H ₂
Mg*C ₉ H ₁₁ Cl	Mg*H ₂
Mg*C ₉ H ₁₇ Br	Mg*I ₂
Mg*C ₁₀ H ₇ Br	Mg*I ₂
Mg*C ₁₀ H ₁₀	Mg*I ₂
Mg*C ₁₀ H ₁₀	Mg*In
Mg*C ₁₀ H ₁₆	MgN*C ₅ H ₄ Br
Mg*C ₁₀ H ₁₈ Cl	MgN*C ₅ H ₇
Mg*C ₁₀ H ₂₂	MgN*C ₈ H ₁₀ Br
Mg*C ₁₁ H ₉ Br	MgN*C ₈ H ₁₀ I
Mg*C ₁₁ H ₉ Cl	MgN*C ₈ H ₂₀ Br
Mg*C ₁₁ H ₉ Cl	MgNO*C ₁₂ H ₁₂ Br
Mg*C ₁₁ H ₁₅ Cl	MgNSn*C ₂₄ H ₃₀ Br
Mg*C ₁₂ H ₁₀	MgN ₂ *C ₇ H ₁₉ Br
Mg*C ₁₂ H ₁₀	MgN ₂ *C ₁₀ H ₁₂
Mg*C ₁₂ H ₁₀	MgN ₂ *C ₁₄ H ₂₀
Mg*C ₁₂ H ₁₀	MgN ₂ *C ₁₆ H ₁₂
Mg*C ₁₂ H ₁₀	MgN ₂ *C ₁₈ H ₂₈
Mg*C ₁₂ H ₁₄	MgN ₂ *C ₂₂ H ₂₀
Mg*C ₁₂ H ₂₆	MgN ₂ Si ₂ *C ₁₂ H ₃₄
Mg*C ₁₃ H ₁₁ Br	MgN ₂ Si ₂ *C ₁₃ H ₃₆
Mg*C ₁₃ H ₁₅ Br	MgNaPb
Mg*C ₁₄ H ₉ Br	MgNaPb
Mg*C ₁₄ H ₁₀	Formation: 5.4.7.1.1
Mg*C ₁₄ H ₁₈	MgO*C ₂ H ₅ Cl
Mg*C ₁₆ H ₁₅ Br	MgO*C ₄ H ₈
Mg*C ₁₆ H ₁₆	MgO*C ₉ H ₁₀
Mg*C ₁₆ H ₂₂	MgO*C ₉ H ₁₄ Br
Mg*C ₁₆ H ₃₀	MgOSi*C ₇ H ₁₇ Cl
Mg*C ₁₆ I ₂ K ₂	MgOSi*C ₁₄ H ₂₉ Br
Mg*C ₁₇ H ₁₅ ClGe	MgOSi ₃ *C ₁₀ H ₂₆
Mg*C ₁₈ H ₁₄	MgO ₂ *C ₇ H ₁₃ Cl

- $\text{MgO}_2 \cdot \text{C}_{12}\text{H}_{18}$
 $\text{MgO}_2\text{S} \cdot \text{C}_9\text{H}_9\text{Br}$
 $\text{MgO}_2\text{S} \cdot \text{C}_{14}\text{H}_{11}\text{Br}$
 $\text{MgO}_2\text{Si}_2 \cdot \text{C}_{14}\text{H}_{34}$
 $\text{MgO}_4 \cdot \text{C}_6\text{H}_{14}$
 $\text{MgO}_4 \cdot \text{C}_{14}\text{H}_{38}\text{Ge}_2$
 $\text{MgPb} \cdot \text{C}_3\text{H}_9\text{Cl}$
 $\text{MgPb} \cdot \text{C}_6\text{H}_{15}\text{Cl}$
 $\text{MgPb} \cdot \text{C}_{15}\text{H}_{33}\text{Cl}$
 $\text{MgPb} \cdot \text{C}_{18}\text{BrF}_{15}$
 $\text{MgPb} \cdot \text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{MgPb} \cdot \text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{MgPb} \cdot \text{C}_{18}\text{H}_{15}\text{Cl}$
 $\text{MgPbSi}_3 \cdot \text{C}_{12}\text{H}_{33}\text{Cl}$
 $\text{MgS} \cdot \text{C}_3\text{H}_4$
 $\text{MgS} \cdot \text{C}_4\text{H}_3\text{Br}$
 $\text{MgS} \cdot \text{C}_4\text{H}_6$
 $\text{MgSi} \cdot \text{C}_4\text{H}_{11}\text{Cl}$
 $\text{MgSi} \cdot \text{C}_5\text{H}_{11}\text{Br}$
 $\text{MgSi} \cdot \text{C}_9\text{H}_{14}$
 $\text{MgSi} \cdot \text{C}_{17}\text{H}_{15}\text{Br}$
 $\text{MgSi} \cdot \text{C}_{17}\text{H}_{22}\text{Br}$
 $\text{MgSi} \cdot \text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{MgSi} \cdot \text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{MgSi}_2 \cdot \text{C}_8\text{H}_{22}$
 $\text{MgSi}_2 \cdot \text{C}_{16}\text{H}_{22}$
MgSn
 MgSn
 Formation: 5.4.6.1
 $\text{MgSn} \cdot \text{C}_3\text{H}_9\text{Br}$
 $\text{MgSn} \cdot \text{C}_{12}\text{H}_{27}\text{Cl}$
 $\text{MgSn} \cdot \text{C}_{16}\text{H}_{15}\text{Br}$
 $\text{MgSn} \cdot \text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{MgSn} \cdot \text{C}_{18}\text{H}_{19}\text{Br}$
 $\text{MgSn}_2 \cdot \text{C}_{36}\text{H}_{30}$
 $\text{MgSn}_2 \cdot \text{C}_{36}\text{H}_{30}$
 $\text{MgZn} \cdot \text{C}_4\text{H}_{12}$
 $\text{MgZn} \cdot \text{C}_4\text{H}_{12}$
 $\text{MgZn} \cdot \text{H}_4$
 $\text{Mg}_2 \cdot \text{CH}_2\text{I}_2$
 $\text{Mg}_2 \cdot \text{CH}_6$
 $\text{Mg}_2 \cdot \text{C}_2\text{Br}_2$
 $\text{Mg}_2 \cdot \text{C}_2\text{H}_5\text{Cl}_3$
 $\text{Mg}_2 \cdot \text{C}_3$
 $\text{Mg}_2 \cdot \text{C}_3\text{H}_4\text{Br}_2$
 $\text{Mg}_2 \cdot \text{C}_3\text{H}_6\text{Br}_2$
 $\text{Mg}_2 \cdot \text{C}_3\text{H}_6\text{Br}_2$
 $\text{Mg}_2 \cdot \text{C}_5\text{H}_{10}\text{Br}_2$
 $\text{Mg}_2 \cdot \text{C}_6\text{H}_4\text{Br}_2$
 $\text{Mg}_2 \cdot \text{C}_6\text{H}_8$
 $\text{Mg}_2 \cdot \text{C}_8\text{H}_{12}\text{Cl}_2$
 $\text{Mg}_2 \cdot \text{C}_8\text{H}_{21}\text{Li}$
 $\text{Mg}_2 \cdot \text{C}_{10}\text{H}_8\text{Br}_2\text{Fe}$
 $\text{Mg}_2 \cdot \text{C}_{10}\text{H}_{20}$
 $\text{Mg}_2 \cdot \text{C}_{16}\text{H}_{16}\text{Cl}_2$
 $\text{Mg}_2 \cdot \text{H}_5\text{Li}$
 $\text{Mg}_2\text{N} \cdot \text{C}_5\text{H}_9$
 $\text{Mg}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{Br}_2$
 $\text{Mg}_2\text{O} \cdot \text{C}_7\text{H}_{12}\text{Br}_2$
Mg₂Sn
 Mg₂Sn
 Formation: 5.4.6.1
 $\text{Mg}_2\text{Sn}_2 \cdot \text{C}_{36}\text{H}_{30}\text{Br}_2$
 $\text{Mg}_3\text{O}_3 \cdot \text{C}_9\text{H}_{18}$
Mg₄Na₂Pb₃
 Mg₄Na₂Pb₃
 Formation: 5.4.7.1.1
 $\text{MnO}_3 \cdot \text{C}_8\text{H}_3\text{B}_2\text{I}_4$
 $\text{MnO}_3 \cdot \text{C}_8\text{H}_4\text{BBr}_2$
 $\text{MnO}_3 \cdot \text{C}_8\text{H}_4\text{BI}_2$
 $\text{MnO}_3 \cdot \text{C}_8\text{H}_5$
 $\text{MnO}_3 \cdot \text{C}_9\text{H}_6\text{BBr}_2$
 $\text{MnO}_3 \cdot \text{C}_9\text{H}_6\text{BI}_2$
 $\text{MnO}_3 \cdot \text{C}_9\text{H}_7$
 $\text{MnO}_3 \cdot \text{C}_9\text{H}_7\text{BI}$
 $\text{MnO}_3 \cdot \text{C}_{10}\text{H}_9\text{BI}$
 $\text{MnO}_3 \cdot \text{C}_{14}\text{H}_9\text{BI}$
 $\text{MnO}_3 \cdot \text{C}_{15}\text{H}_{11}\text{BI}$
N*CH
N*CK
N*C₂H₈Al
N*C₃H₄I
N*C₃H₆Al
N*C₃H₁₁ClGa
N*C₃H₁₂Al
N*C₃H₁₂Ga
N*C₃H₁₂Ga
N*C₄H₄
N*C₄H₆B
N*C₄H₉Ge
N*C₄H₁₀BCl
N*C₄H₁₂D₂Ga
N*C₄H₁₄Al
N*C₄H₁₄Ga
N*C₅H₄BrMg
N*C₅H₅
N*C₅H₆BCl₂
N*C₅H₇Mg
N*C₅H₉Mg₂
N*C₅H₁₀Al
N*C₅H₁₄B
N*C₅H₁₅Be
N*C₅H₁₅DGa
N*C₅H₁₆Al

$N^*C_5H_{16}Al$	$NSi^*C_{40}H_{42}B$
$N^*C_5H_{16}Ga$	$NSi_3^*C_9H_{12}7$
$N^*C_6H_{15}BCl$	$NSi_4^*C_{50}H_{46}B$
$N^*C_6H_{15}BeLi$	$NSn^*C_4H_9$
$N^*C_6H_{18}Al$	$NSn^*C_4H_{19}BCl$
$N^*C_6H_{18}Ga$	$NSn^*C_2H_{30}BrMg$
$N^*C_6H_{18}Ga$	$NSn_2^*C_{10}H_{28}B$
$N^*C_7H_{11}Be$	$NSr^*C_{16}H_{16}$
$N^*C_7H_{20}Al$	$NTl^*C_{32}H_{20}F_{20}$
$N^*C_7H_{33}B_{18}$	$N_2^*CH_2$
$N^*C_8H_7$	$N_2^*CH_2$
$N^*C_8H_{10}BrMg$	$N_2^*CH_2$
$N^*C_8H_{10}IMg$	$N_2^*C_2H_4BCl$
$N^*C_8H_{10}Li$	$N_2^*C_3H_6BCl$
$N^*C_8H_{11}$	$N_2^*C_4H_6GaK$
$N^*C_8H_{20}BrMg$	$N_2^*C_4H_{10}BCl$
$N^*C_9H_{15}Be$	$N_2^*C_4H_{12}BCl$
$N^*C_9H_{18}Al$	$N_2^*C_4H_{12}BCl$
$N^*C_9H_{18}Al$	$N_2^*C_4H_{12}Be$
$N^*C_9H_{18}Al$	$N_2^*C_4H_{18}B_{10}$
$N^*C_9H_{18}Li$	$N_2^*C_5H_{12}$
$N^*C_9H_{23}Be$	$N_2^*C_6H_4BClF_4$
$N^*C_9H_{24}Al$	$N_2^*C_6H_5BF_4$
$N^*C_{10}H_{26}Al$	$N_2^*C_6H_8In$
$N^*C_{11}H_{14}Al$	$N_2^*C_6H_{20}Be_2$
$N^*C_{11}H_{15}$	$N_2^*C_6H_{22}B_{10}$
$N^*C_{11}H_{16}B$	$N_2^*C_7H_7BF_4$
$N^*C_{11}H_{22}BeCl$	$N_2^*C_7H_{19}BrMg$
$N^*C_{12}H_{18}Al$	$N_2^*C_8H_9BF_4$
$N^*C_{12}H_{30}Al$	$N_2^*C_8H_{20}BCl$
$N^*C_{13}H_{31}Be$	$N_2^*C_8H_{21}BeBr$
$N^*C_{13}H_{31}Be$	$N_2^*C_8H_{21}Br_2In$
$N^*C_{14}H_{14}Al$	$N_2^*C_8H_{21}Ga$
$N^*C_{14}H_{16}Al$	$N_2^*C_8H_{24}Be_2$
$N^*C_{14}H_{16}B$	$N_2^*C_8H_{24}In_2$
$N^*C_{16}H_{16}Ba$	$N_2^*C_8H_{26}Be_2$
$N^*C_{16}H_{16}Ca$	$N_2^*C_{10}H_8$
$N^*C_{17}H_{16}B$	$N_2^*C_{10}H_{12}Mg$
$N^*C_{25}H_{22}Al$	$N_2^*C_{10}H_{26}Be$
$N^*C_{25}H_{22}Al$	$N_2^*C_{11}H_{27}BeBr$
$N^*C_{27}H_{24}Al$	$N_2^*C_{11}H_{27}Ga$
$N^*C_{29}H_{20}Al$	$N_2^*C_{11}H_{30}Ga_2$
NNa^*C	$N_2^*C_{12}H_{11}BeCl$
$NNa_2^*CH_{13}B_{10}$	$N_2^*C_{12}H_{17}CaI$
$NO^*C_4H_{17}B_{10}$	$N_2^*C_{12}H_{29}Al$
$NO^*C_{12}H_{12}BrMg$	$N_2^*C_{12}H_{30}Be$
$NO^*C_{14}H_{16}B$	$N_2^*C_{12}H_{32}B_{10}Br_{10}$
$NO^*C_{16}H_{22}B$	$N_2^*C_{13}H_{10}$
$NPb^*C_4H_9$	$N_2^*C_{14}H_{20}Mg$
$NSi^*C_4H_9$	$N_2^*C_{14}H_{30}Be_2$
$NSi^*C_8H_{15}$	$N_2^*C_{16}H_{12}Mg$
$NSi^*C_{24}H_{30}B$	$N_2^*C_{16}H_{38}B_2$

$N_2^*C_{16}H_{42}B_2$	Reaction with $Hg(SiR_3)_2$ and $(R_3Si)_3^*$
$N_2^*C_{16}H_{42}Be_2$	$Al \cdot OEt_2$: 5.3.8.5
$N_2^*C_{17}H_{42}Ga_2$	Reaction with PbR_4 : 5.4.7.2.3
$N_2^*C_{18}H_{28}Mg$	Na^*AlH_4
$N_2^*C_{18}H_{30}Be_2$	$Na^*B_{10}H_{13}$
$N_2^*C_{18}H_{42}B_2$	$Na^*CH_3AlCl_3$
$N_2^*C_{20}H_{42}B_2$	$Na^*CH_{11}B_{10}$
$N_2^*C_{20}H_{42}Be_2$	Na^*CN
$N_2^*C_{20}H_{46}B_2$	Na^*C_2H
$N_2^*C_{22}H_{20}Mg$	$Na^*C_2H_6AlF_2$
$N_2^*C_{22}H_{50}Al_2$	$Na^*C_2H_7B_4$
$N_2^*C_{26}H_{54}B_2$	$Na^*C_2H_7B_4$
$N_2^*C_{30}H_{54}Be_2$	$Na^*C_2H_7B_4$
$N_2^*CaH_4$	$Na^*C_2H_7B_4$
$N_2O^*C_7H_7BF_4$	$Na^*C_2H_{11}B_9$
$N_2O^*C_8H_9BF_4$	$Na^*C_4H_9$
$N_2O^*C_{12}H_{16}Be$	$Na^*C_4H_{11}B_4$
$N_2O^*C_{15}H_{22}Be$	$Na^*C_4H_{11}B_4$
$N_2O_2^*C_4H_6$	$Na^*C_4H_{11}Be$
$N_2O_2S^*C_6H_{20}$	$Na^*C_4H_{12}Al$
$N_2O_3Si^*C_{13}H_{33}B$	$Na^*C_4H_{12}Al$
$N_2P_2Si^*C_8H_{24}$	$Na^*C_4H_{14}Al_2$
$N_2P_2Si^*C_{14}H_{42}Al_2$	$Na^*C_5H_5$
$N_2Pb^*C_7H_{19}B$	$Na^*C_6H_5$
$N_2Si^*C_7H_{21}B$	$Na^*C_6H_{12}Al$
$N_2Si^*C_{22}H_{27}B$	$Na^*C_6H_{16}Al$
$N_2Si_2^*C_{12}H_{34}Mg$	$Na^*C_6H_{16}Al$
$N_2Si_2^*C_{13}H_{36}Mg$	$Na^*C_6H_{16}B$
$N_2Si_6^*C_{24}H_{70}Al_2$	$Na^*C_8H_{20}Al$
$N_2Sn^*C_4H_{12}$	$Na^*C_8H_{21}B_8Fe$
$N_2Sn^*C_6H_{15}B$	$Na^*C_9H_{18}B$
$N_2Sn^*C_{11}H_{29}B$	$Na^*C_{10}H_8$
$N_2Sn_2^*C_{10}H_{30}B_2$	$Na^*C_{10}H_8$
$N_2Ti^*C_2H_7$	$Na^*C_{12}H_{14}Al$
$N_2Ti^*C_6H_8I$	$Na^*C_{12}H_{18}Al$
$N_3^*C_3B_{10}Cl_7Cs_2$	$Na^*C_{12}H_{28}Al$
$N_3^*C_3H_9B_3Cl_3$	$Na^*C_{19}H_{15}$
$N_3^*C_6H_{18}B$	$Na^*C_{24}H_{20}Al$
$N_3^*C_9H_{27}Be_3$	$Na^*C_{24}H_{20}B$
$N_3^*C_{18}H_{15}B_3Cl_3$	$Na^*C_{24}H_{36}Al$
$N_3OP^*C_6H_{18}$	$Na^*C_{24}H_{52}Ga$
N_3O_9Ti	$Na^*C_{28}H_{60}Ga$
$Tl(NO_3)_3$	$Na^*C_{31}H_{25}Be$
Thallating agent: 5.3.6.3.4	$Na^*C_{32}H_{68}Ga$
$N_3Si_3^*C_{72}H_{60}B_3$	Na^*Cl
$N_4^*B_{10}H_8$	Na^*F
$N_4^*C_4HgK_2$	Na^*GaH_4
$N_4^*C_8H_{24}B_2$	Na^*H
$N_4^*C_{10}H_{16}$	$NaO_4^*C_6H_{15}Al$
$N_4^*C_{12}H_{24}Ga_4$	$NaO_4^*C_{16}H_{12}Al$
Na	$NaO_8Si_4^*C_{44}H_{116}Al$
Na	$NaPb^*Mg$
Dehalogenation of R_2AlX , $RAlX_2$:	
5.3.3.3.4	

- $\text{NaS}_4^*\text{C}_{16}\text{H}_{12}\text{Al}$
 $\text{NaSi}_4^*\text{C}_{12}\text{H}_{36}\text{Al}$
 $\text{NaSi}_4^*\text{C}_{12}\text{H}_{36}\text{Al}$
 $\text{NaSi}_4^*\text{C}_{26}\text{H}_{52}\text{Al}$
NaTi
 Na-Ti alloy
 Reaction with $[\text{RN}_2][\text{BF}_4]$: 5.3.6.2.5
 Reaction with RX: 5.3.6.2.1
 $\text{NaZn}^*\text{C}_2\text{H}_7$
 $\text{NaZn}_2^*\text{H}_5$
 $\text{Na}_2^*\text{CH}_{13}\text{B}_{10}\text{N}$
 $\text{Na}_2^*\text{C}_2\text{H}_{11}\text{B}_9$
 $\text{Na}_2^*\text{C}_8\text{H}_{12}$
 $\text{Na}_2^*\text{C}_{10}\text{H}_8\text{Fe}$
 $\text{Na}_2^*\text{C}_{14}\text{H}_{30}\text{Al}_2$
 $\text{Na}_2^*\text{C}_{16}\text{H}_{16}$
 $\text{Na}_2^*\text{C}_{26}\text{H}_{54}\text{Al}_2$
 $\text{Na}_2\text{Pb}_3^*\text{Mg}_4$
 $\text{Na}_3^*\text{AlF}_6$
 Ni^*Cl_2
 $\text{NiP}_2^*\text{C}_{36}\text{H}_{30}\text{Cl}_2$
 $\text{NiP}_4^*\text{C}_{72}\text{H}_{60}$
 O^*C
 O^*C
 O^*C
 $\text{O}^*\text{CH}_3\text{B}$
 $\text{O}^*\text{CH}_3\text{Ga}$
 $\text{O}^*\text{CH}_7\text{B}_3$
 $\text{O}^*\text{CH}_8\text{B}_4$
 $\text{O}^*\text{CH}_{13}\text{B}_9$
 $\text{O}^*\text{C}_2\text{H}_5\text{ClMg}$
 $\text{O}^*\text{C}_2\text{H}_7\text{Ga}$
 $\text{O}^*\text{C}_2\text{H}_{13}\text{B}_3$
 $\text{O}^*\text{C}_4\text{H}_4$
 $\text{O}^*\text{C}_4\text{H}_8\text{Mg}$
 $\text{O}^*\text{C}_4\text{H}_9\text{Cu}$
 $\text{O}^*\text{C}_4\text{H}_{10}$
 $\text{O}^*\text{C}_4\text{H}_{10}\text{BCl}$
 $\text{O}^*\text{C}_4\text{H}_{10}\text{BF}_3$
 $\text{O}^*\text{C}_4\text{H}_{11}\text{Al}$
 $\text{O}^*\text{C}_4\text{H}_{11}\text{B}$
 $\text{O}^*\text{C}_4\text{H}_{11}\text{BCl}_2$
 $\text{O}^*\text{C}_4\text{H}_{12}\text{AlCl}$
 $\text{O}^*\text{C}_4\text{H}_{12}\text{BCl}$
 $\text{O}^*\text{C}_4\text{H}_{12}\text{BCl}$
 $\text{O}^*\text{C}_4\text{H}_{13}\text{Al}$
 $\text{O}^*\text{C}_4\text{H}_{14}\text{B}_{10}$
 $\text{O}^*\text{C}_4\text{H}_{17}\text{B}_{10}\text{N}$
 $\text{O}^*\text{C}_5\text{H}_{11}\text{B}$
 $\text{O}^*\text{C}_6\text{H}_{12}\text{Br}_2\text{Mg}_2$
 $\text{O}^*\text{C}_6\text{H}_{13}\text{BaI}$
 $\text{O}^*\text{C}_6\text{H}_{15}\text{BF}_4$
 $\text{O}^*\text{C}_6\text{H}_{21}\text{B}_9\text{Be}$
 $\text{O}^*\text{C}_7\text{H}_5\text{Cl}$
 $\text{O}^*\text{C}_7\text{H}_7\text{BF}_4\text{N}_2$
 $\text{O}^*\text{C}_7\text{H}_7\text{CaI}$
 $\text{O}^*\text{C}_7\text{H}_8$
 $\text{O}^*\text{C}_7\text{H}_{12}\text{Br}_2\text{Mg}_2$
 $\text{O}^*\text{C}_7\text{H}_{15}\text{Al}$
 $\text{O}^*\text{C}_7\text{H}_{15}\text{B}$
 $\text{O}^*\text{C}_7\text{H}_{17}\text{Al}$
 $\text{O}^*\text{C}_7\text{H}_{19}\text{Al}$
 $\text{O}^*\text{C}_7\text{H}_{19}\text{Ga}$
 $\text{O}^*\text{C}_7\text{H}_{19}\text{In}$
 $\text{O}^*\text{C}_8\text{H}_9\text{BF}_4\text{N}_2$
 $\text{O}^*\text{C}_8\text{H}_{10}$
 $\text{O}^*\text{C}_8\text{H}_{18}$
 $\text{O}^*\text{C}_8\text{H}_{19}\text{Al}$
 $\text{O}^*\text{C}_9\text{H}_{10}\text{Mg}$
 $\text{O}^*\text{C}_9\text{H}_{14}\text{BrMg}$
 $\text{O}^*\text{C}_9\text{H}_{17}\text{B}$
 $\text{O}^*\text{C}_9\text{H}_{21}\text{B}$
 $\text{O}^*\text{C}_{10}\text{H}_{13}\text{Al}$
 $\text{O}^*\text{C}_{10}\text{H}_{17}\text{Al}$
 $\text{O}^*\text{C}_{10}\text{H}_{19}\text{Al}$
 $\text{O}^*\text{C}_{10}\text{H}_{22}$
 $\text{O}^*\text{C}_{10}\text{H}_{23}\text{Al}$
 $\text{O}^*\text{C}_{10}\text{H}_{25}\text{Ga}$
 $\text{O}^*\text{C}_{11}\text{H}_{19}\text{Al}$
 $\text{O}^*\text{C}_{11}\text{H}_{25}\text{B}$
 $\text{O}^*\text{C}_{12}\text{H}_{11}\text{B}$
 $\text{O}^*\text{C}_{12}\text{H}_{12}\text{BrMgN}$
 $\text{O}^*\text{C}_{12}\text{H}_{16}\text{BeN}_2$
 $\text{O}^*\text{C}_{12}\text{H}_{17}\text{B}$
 $\text{O}^*\text{C}_{12}\text{H}_{27}\text{Al}$
 $\text{O}^*\text{C}_{12}\text{H}_{28}\text{Be}$
 $\text{O}^*\text{C}_{13}\text{H}_{19}\text{Al}$
 $\text{O}^*\text{C}_{13}\text{H}_{21}\text{B}$
 $\text{O}^*\text{C}_{13}\text{H}_{30}\text{B}_2$
 $\text{O}^*\text{C}_{13}\text{H}_{31}\text{Al}$
 $\text{O}^*\text{C}_{13}\text{H}_{35}\text{AlGe}_3$
 $\text{O}^*\text{C}_{14}\text{H}_{15}\text{B}$
 $\text{O}^*\text{C}_{14}\text{H}_{16}\text{BN}$
 $\text{O}^*\text{C}_{14}\text{H}_{23}\text{B}$
 $\text{O}^*\text{C}_{15}\text{H}_{22}\text{BeN}_2$
 $\text{O}^*\text{C}_{15}\text{H}_{25}\text{B}$
 $\text{O}^*\text{C}_{16}\text{H}_{19}\text{B}$
 $\text{O}^*\text{C}_{16}\text{H}_{22}\text{BN}$
 $\text{O}^*\text{C}_{16}\text{H}_{37}\text{Al}$
 $\text{O}^*\text{C}_{18}\text{H}_{35}\text{B}$
 $\text{O}^*\text{C}_{19}\text{H}_{43}\text{Al}$
 $\text{O}^*\text{C}_{20}\text{H}_{15}\text{B}$
 $\text{O}^*\text{C}_{20}\text{H}_{20}\text{Be}$
 $\text{O}^*\text{C}_{21}\text{H}_{21}\text{Ga}$

$O^*C_{22}H_{10}F_{15}Ga$
 $O^*C_{22}H_{10}F_{15}In$
 $O^*C_{22}H_{24}Ge$
 $O^*C_{22}H_{25}Al$
 $O^*C_{28}H_{25}Al$
 $O^*C_{38}H_{35}Al$
 $O^*C_{40}H_{38}BaGe_2$
 $O^*C_{42}H_{38}Ca$
 O^*D_2
 O^*H_2
 $OP^*C_6H_{18}N_3$
 $OP_2^*C_{37}H_{30}ClIr$
 $OS^*C_3H_{14}B_{10}$
 $OS^*C_4H_{11}B$
 $OS^*C_6H_5B$
 $OSi^*C_7H_{17}Cl$
 $OSi^*C_7H_{17}ClMg$
 $OSi^*C_{14}H_{29}BrMg$
 $OSi^*C_{14}H_{29}Li$
 $OSi_2^*C_6H_{18}$
 $OSi_2^*C_{10}H_{26}Mg$
 $OSi_3^*C_{13}H_{35}Al$
 $OSi_3^*C_{13}H_{35}Al$
 $OSi_3^*C_{13}H_{35}Ga$
 $OSi_3^*C_{13}H_{37}Al$
 $OSi_4^*C_{18}H_{48}AlCl$
 $OSn_3^*C_{13}H_{35}Al$
 $OSr^*C_{40}H_{38}Ge_2$
 O_2

O_2

Reaction with RMgX: 5.4.2.5

$O_2^*B_{12}$
 $O_2^*B_{12}H_{18}$
 O_2^*C
 $O_2^*CH_3BCl_2$
 $O_2^*C_2H_4BCl$
 $O_2^*C_2H_5B$
 $O_2^*C_2H_6$
 $O_2^*C_2H_6BCl$
 $O_2^*C_2H_6BCl$
 $O_2^*C_2H_7In$
 $O_2^*C_2H_8B_{10}$
 $O_2^*C_2H_{10}B_{12}$
 $O_2^*C_3H_7B$
 $O_2^*C_3H_9B$
 $O_2^*C_4H_6N_2$
 $O_2^*C_4H_7B$
 $O_2^*C_4H_{10}Ba$
 $O_2^*C_4H_{10}Be$
 $O_2^*C_4H_{10}Ca$
 $O_2^*C_4H_{11}B$
 $O_2^*C_5H_{11}BeBr$

$O_2^*C_5H_{11}BeCl$
 $O_2^*C_6H_5B$
 $O_2^*C_6H_{13}B$
 $O_2^*C_7H_6$
 $O_2^*C_7H_9B$
 $O_2^*C_7H_{13}ClMg$
 $O_2^*C_7H_{15}B$
 $O_2^*C_8H_{17}B$
 $O_2^*C_8H_{18}B_{10}$
 $O_2^*C_8H_{18}Be$
 $O_2^*C_8H_{19}B$
 $O_2^*C_8H_{19}BeBr$
 $O_2^*C_8H_{19}BeCl$
 $O_2^*C_9H_{15}B$
 $O_2^*C_9H_{24}Be$
 $O_2^*C_{10}H_{13}BeCl$
 $O_2^*C_{10}H_{13}CaI$
 $O_2^*C_{10}H_{19}B$
 $O_2^*C_{10}H_{21}B$
 $O_2^*C_{10}H_{26}Be$
 $O_2^*C_{11}H_{15}CaI$
 $O_2^*C_{11}H_{21}B$
 $O_2^*C_{12}H_{15}B$
 $O_2^*C_{12}H_{18}Mg$
 $O_2^*C_{12}H_{21}B$
 $O_2^*C_{12}H_{25}B$
 $O_2^*C_{12}H_{30}Be$
 $O_2^*C_{13}H_{17}B$
 $O_2^*C_{13}H_{21}CaI$
 $O_2^*C_{14}H_{23}B$
 $O_2^*C_{14}H_{23}B$
 $O_2^*C_{14}H_{26}Be$
 $O_2^*C_{14}H_{28}B_{10}$
 $O_2^*C_{16}H_{25}B$
 $O_2^*C_{16}H_{30}Be$
 $O_2^*C_{16}H_{38}Be_2K_2$
 $O_2^*C_{17}H_{25}B$
 $O_2^*C_{18}H_{26}Ca$
 $O_2^*C_{19}H_{16}Ge$
 $O_2^*C_{20}H_{26}Ca$
 $O_2^*C_{20}H_{28}BLi$
 $O_2^*C_{21}H_{25}CaCl$
 $O_2^*C_{22}H_{30}Ca$
 $O_2^*C_{24}H_{26}Be$
 $O_2^*C_{26}H_{30}Ca$
 $O_2^*C_{27}H_{31}CaCl$
 $O_2^*C_{28}H_{30}Ca$
 $O_2^*C_{34}H_{34}Ca$
 $O_2P_4^*C_{10}H_{32}B_2Be$
 $O_2S^*C_4H_7B$
 $O_2S^*C_8H_{20}N_2$
 $O_2S^*C_9H_9BrMg$

$O_2S^*C_9H_9Li$
 $O_2S^*C_{14}H_{11}BrMg$
 $O_2S^*C_{14}H_{11}Li$
 O_2Si

SiO_2

Reaction with elemental boron: 5.3.7.1

$O_2Si^*C_4H_{15}Al$
 $O_2Si_2^*C_{14}H_{34}Mg$
 $O_2Sr^*C_4H_{10}$
 $O_2Sr^*C_9H_{19}I$
 $O_2Sr^*C_{10}H_{21}I$
 $O_2Sr^*C_{11}H_{23}I$
 $O_2Sr^*C_{12}H_{25}I$
 $O_2Ti^*C_6H_{13}$
 $O_2Ti^*C_7H_{15}$
 $O_2Ti^*C_8H_{17}$
 $O_2Ti^*C_{11}H_{15}$
 $O_2Ti^*C_{14}H_{14}BF_4$
 $O_2Ti^*C_{16}H_{18}BF_4$
 $O_2Zn^*C_4H_{10}$
 $O_3^*BH_3$
 $O_3^*B_2$
 $O_3^*C_3H_9B_4Fe$
 $O_3^*C_3H_9Al$
 $O_3^*C_3H_9B$
 $O_3^*C_3H_9B$
 $O_3^*C_4H_5B$
 $O_3^*C_6H_7B$
 $O_3^*C_6H_{15}B$
 $O_3^*C_6H_{21}Ge_3$
 $O_3^*C_8H_3B_2I_4Mn$
 $O_3^*C_8H_4BBR_2Mn$
 $O_3^*C_8H_4BI_2Mn$
 $O_3^*C_8H_5Mn$
 $O_3^*C_8H_{17}B$
 $O_3^*C_9H_6BBR_2Mn$
 $O_3^*C_9H_6BI_2Mn$
 $O_3^*C_9H_6Cr$
 $O_3^*C_9H_7BIMn$
 $O_3^*C_9H_7Mn$
 $O_3^*C_9H_{18}Mg_3$
 $O_3^*C_9H_{22}BK$
 $O_3^*C_{10}H_9BIMn$
 $O_3^*C_{12}H_{27}B$
 $O_3^*C_{14}H_9BIMn$
 $O_3^*C_{15}H_{11}BIMn$
 $O_3^*C_{21}H_{21}Ga$
 $O_3^*C_{21}H_{21}In$
 $O_3P^*C_3H_9$
 O_3S^*FH
 $O_3Si^*C_{13}H_{33}BN_2$
 $O_3Si_4^*C_{24}H_{66}AlK$

$O_3Si_4^*C_{24}H_{66}AlLi$
 $O_3Si_4^*C_{24}H_{66}GaLi$
 $O_3Ti^*C_{21}H_9F_{12}$
 $O_4^*C_4H_{12}B_2$
 $O_4^*C_5H_{14}B_2$
 $O_4^*C_5H_{14}B_2$
 $O_4^*C_6H_{14}Mg$
 $O_4^*C_6H_{15}AlNa$
 $O_4^*C_6H_{16}B_2$
 $O_4^*C_8H_{14}BrIn$
 $O_4^*C_8H_{24}Be_4$
 $O_4^*C_8H_{28}Ga_4$
 $O_4^*C_{10}H_{24}B_2$
 $O_4^*C_{14}H_{38}Ge_2Mg$
 $O_4^*C_{16}H_{12}AlNa$
 $O_4^*C_{20}H_{46}Be_2Li_2$
 $O_4^*C_{20}H_{48}Be_4$
 $O_4^*C_{22}H_{15}CoGe$
 $O_4^*C_{40}H_{74}Al_4$
 $O_4Pb^*C_4H_6$
 $O_4S^*C_2H_6$
 $O_4Si^*C_{21}H_{15}Co$
 $O_4Si^*C_{22}H_{15}Co$
 $O_4Si_4^*C_4H_{12}Cl_4$
 $O_4Si_4^*C_8H_{24}$
 $O_4Si_4^*C_{28}H_{78}AlLi$
 $O_4Ti^*C_8H_{20}$
 $O_4Ti^*C_{16}H_{36}$
 $O_4Ti^*C_5H_9$
 $O_4Ti^*C_{11}H_7F_6$
 $O_5Ti^*C_{11}H_{15}F_6$
 $O_5Ti^*C_{11}H_{21}$
 $O_6^*C_3H_9B_3$
 $O_6^*C_7H_{19}B_3$
 $O_6^*C_9H_{18}B_2$
 $O_6^*C_{10}H_6Co_2$
 $O_6^*C_{12}H_{27}B_3$
 $O_6^*C_{18}H_{15}B_3$
 $O_6^*C_{18}H_{33}B_3$
 $O_6^*C_{24}H_{54}Be_3$
 $O_6S_2Ti^*C_8F_{11}$
 $O_6S_2Ti^*C_9HF_{10}$
 $O_6S_2Ti^*C_9H_2F_9$
 $O_6S_2Ti^*C_9H_3F_{10}$
 $O_6Ti^*C_3Cl_9$
 $O_6Ti^*C_6F_9$
 $O_6Ti^*C_6F_9$
 $O_6Ti^*C_6H_9$
 $O_6Ti^*C_{12}H_{21}$
 $O_7S_2Ti^*C_9H_3F_{10}$
 $O_8^*C_9H_{24}B_4$
 $O_8Si_4^*C_{44}H_{116}AlNa$

$O_9S_3Ti^*C_3F_9$
 $O_9Ti^*N_3$
 $O_{12}Ti^*Cl_3$
 $P^*C_3H_9O_3$
 $P^*C_4H_{10}Li$
 $P^*C_6H_{18}N_3O$
 $P^*C_7H_{20}In$
 $P^*C_{36}H_{15}F_{15}In$
 $PSi^*C_{26}H_{36}Ga$
 $PSi_3^*C_9H_{27}$
 $PSi_6^*C_{18}H_{54}Al$
 $P_2^*B_{12}$
 $P_2^*C_{12}H_{32}In_2$
 $P_2^*C_{36}H_{30}Cl_2Ni$
 $P_2^*C_3H_{30}ClIrO$
 $P_2Si^*C_8H_{24}N_2$
 $P_2Si^*C_{14}H_{42}Al_2N_2$
 $P_4^*C_{10}H_{32}B_2BeO_2$
 $P_4^*C_{12}H_{36}B_2Be$
 $P_4^*C_{52}H_{48}B_2Br_4Co$
 $P_4^*C_{72}H_{60}Ni$
 $P_4^*C_{76}H_{68}B_2Co$
 $P_6Sn^*C_{81}H_{81}BBR_2$
 $P_8Sn^*C_{105}H_{99}B_2Br_2$
Pb

Pb

Alloy formation: 5.4.7.1.1
 Reaction with Ba metal: 5.4.7.1.1
 Reaction with Ca metal: 5.4.7.1.1
 Reaction with $CaCl_2$: 5.4.7.1.2
 Reaction with CaC_2 : 5.4.7.1.2
 Reaction with Sr metal: 5.4.7.1.1
 Reaction with group-IIA metals:
 5.4.7.1.3

Pb^*Ba
 Pb^*Ba_2
 Pb^*Br_2
 Pb^*Br_2
 $Pb^*C_2H_6B_4$
 $Pb^*C_2H_{11}B_9$
 $Pb^*C_3H_9Cl$
 $Pb^*C_3H_9ClMg$
 $Pb^*C_3H_9Li$
 $Pb^*C_3H_{17}B_5$
 $Pb^*C_4H_6O_4$
 $Pb^*C_4H_9N$
 $Pb^*C_4H_{10}B_4$
 $Pb^*C_5H_{16}B_4$
 $Pb^*C_6H_{15}Br$
 $Pb^*C_6H_{15}ClMg$
 $Pb^*C_7H_{19}BN_2$
 $Pb^*C_8H_{20}$

$Pb^*C_{15}H_{33}ClMg$
 $Pb^*C_{18}BrF_{15}Mg$
 $Pb^*C_{18}H_{15}BrMg$
 $Pb^*C_{18}H_{15}BrMg$
 $Pb^*C_{18}H_{15}ClMg$
 $Pb^*C_{24}H_{20}$
 $Pb^*C_{25}H_{22}$
 Pb^*Ca
 Pb^*Ca_2
 Pb^*Cl_2
 Pb^*MgNa
 $PbSi_3^*C_{12}H_{33}ClMg$
PbSr
 $SrPb$
 Formation: 5.4.7.1.1
PbSr₂
 Sr_2Pb
 Formation: 5.4.7.1.1
 $Pb_2^*C_{36}H_{30}$
 Pb_3^*Ba
 $Pb_3^*Ba_5$
 Pb_3^*Ca
 $Pb_3^*Ca_5$
 $Pb_3^*Mg_4Na_2$
Pb₃Sr
 $SrPb_3$
 Formation: 5.4.7.1.1
Pb₃Sr₂
 Sr_2Pb_3
 Formation: 5.4.7.1.1
Pb₃Sr₅
 Sr_5Pb_3
 Formation: 5.4.7.1.1
Pb₄Sr₅
 Sr_5Pb_4
 Formation: 5.4.7.1.1
 $Pb_5^*Ba_3$
Pb₅Sr₃
 Sr_3Pb_5
 Formation: 5.4.7.1.1
 $PdSn_3^*Ba$
Pt
Pt
 Use as an anode: 5.3.6.2.9
 S^*B_{12}
 $S^*C_2H_6O_4$
 $S^*C_2H_7BBR_2$
 $S^*C_2H_7BCl_2$
 $S^*C_2H_7BI_2$
 $S^*C_2H_8BBR$
 $S^*C_2H_8BCl$
 $S^*C_2H_8BI$

$S^*C_2H_9B$
 $S^*C_2H_{18}B_{10}$
 $S^*C_3H_4Li_2$
 $S^*C_3H_4Mg$
 $S^*C_3H_{14}B_{10}O$
 $S^*C_4H_3BCl_2$
 $S^*C_4H_3BrMg$
 $S^*C_4H_3Cl_2Ga$
 $S^*C_4H_3Li$
 $S^*C_4H_4$
 $S^*C_4H_4$
 $S^*C_4H_6Li_2$
 $S^*C_4H_6Mg$
 $S^*C_4H_7BO_2$
 $S^*C_4H_{10}$
 $S^*C_4H_{11}B$
 $S^*C_4H_{11}BO$
 $S^*C_6H_5BO$
 $S^*C_6H_{10}B_2I_2$
 $S^*C_7H_{14}BBr_2Cl$
 $S^*C_7H_{19}Ga$
 $S^*C_8H_{17}BBr_2$
 $S^*C_8H_{19}BBr_2$
 $S^*C_8H_{20}BCl$
 $S^*C_8H_{20}N_2O_2$
 $S^*C_8H_{28}B_{10}$
 $S^*C_9H_9BrMgO_2$
 $S^*C_9H_9LiO_2$
 $S^*C_{10}H_{23}BCl_2$
 $S^*C_{14}H_{11}BrMgO_2$
 $S^*C_{14}H_{11}LiO_2$
 S^*FHO_3
 $SSr^*C_4H_3I$
 $S_2^*C_4H_{10}Be$
 $S_2^*C_4H_{24}B_{10}$
 $S_2^*C_8H_{18}Be$
 $S_2^*C_8H_{32}B_{10}$
 $S_2Ti^*C_8F_{11}O_6$
 $S_2Ti^*C_8HF_{10}O_6$
 $S_2Ti^*C_8H_2F_9O_6$
 $S_2Ti^*C_9H_3F_{10}O_6$
 $S_2Ti^*C_9H_3F_{10}O_7$
 $S_3^*B_3I_3$
 $S_3Ti^*C_3F_9O_9$
 $S_4^*C_{16}H_{12}AlNa$
 $S_4^*C_{16}H_{40}Be_4$
 $S_4Sn^*C_{16}H_{12}$
 $Sb^*C_{10}H_{25}$
 $Sb^*C_{16}H_{40}Al$
 $Sb^*C_{22}H_{55}Al_2$
 Sb^*F_3
 Sb^*F_5

Si

Si

Reaction with SiX_4 : 5.3.7.2Reaction with B_2O_3 : 5.3.7.1Reaction with B_2F_4 : 5.3.7.2

Si^*BCl_5
 $Si^*B_2F_6$
 Si^*B_3
 $Si^*B_3F_7$
 Si^*B_4
 Si^*B_6
 Si^*B_{16}
 Si^*B_{50}
 Si^*C
 $Si^*CH_2Cl_4$
 $Si^*CH_4Cl_2$
 $Si^*CH_{10}B_5Cl_3$
 $Si^*CH_{20}B_{10}$
 $Si^*C_2H_6Cl_2$
 $Si^*C_2H_7B_3$
 $Si^*C_2H_{10}B_4$
 $Si^*C_3H_9B_3$
 $Si^*C_3H_9Cl$
 $Si^*C_3H_9Cl$
 $Si^*C_3H_9Cl$
 $Si^*C_3H_9Li$
 $Si^*C_3H_{10}$
 $Si^*C_3H_{16}B_5Cl$
 $Si^*C_3H_{22}B_{10}$
 $Si^*C_4H_8Cl_2$
 $Si^*C_4H_9N$
 $Si^*C_4H_{11}Br_2Ga$
 $Si^*C_4H_{11}Cl$
 $Si^*C_4H_{11}Cl$
 $Si^*C_4H_{11}ClMg$
 $Si^*C_4H_{11}Cl_2Ga$
 $Si^*C_4H_{11}Cl_2In$
 $Si^*C_4H_{12}$
 $Si^*C_4H_{15}AlO_2$
 $Si^*C_4H_{16}B_8$
 $Si^*C_4H_{16}B_8$
 $Si^*C_5H_{11}BrMg$
 $Si^*C_5H_{12}$
 $Si^*C_5H_{14}$
 $Si^*C_5H_{15}B_4Cl$
 $Si^*C_5H_{16}B_4$
 $Si^*C_5H_{16}B_4$
 $Si^*C_5H_{22}B_6$
 $Si^*C_6H_{12}$
 $Si^*C_6H_{15}Cl$
 $Si^*C_6H_{16}$
 $Si^*C_7H_{12}$

Si*C ₇ H ₁₇ ClMgO	Si*Cl ₄
Si*C ₇ H ₁₇ ClO	Si*F ₂
Si*C ₇ H ₂₀ B ₄	Si*F ₂
Si*C ₇ H ₂₁ BN ₂	Si*F ₄
Si*C ₈ H ₁₁ Li	Si*F ₄
Si*C ₈ H ₁₅ N	Si*F ₆ K ₂
Si*C ₈ H ₁₈	Si*H ₃ K
Si*C ₈ H ₂₀	Si*O ₂
Si*C ₈ H ₂₁ Al	SiSn*C ₈ H ₁₆
Si*C ₈ H ₂₁ AlClK	Si ₂ *BF ₇
Si*C ₈ H ₂₁ Ga	Si ₂ *C ₆ H ₁₈
Si*C ₈ H ₂₄ N ₂ P ₂	Si ₂ *C ₆ H ₁₈ Hg
Si*C ₉ H ₁₄	Si ₂ *C ₆ H ₁₈ Hg
Si*C ₉ H ₁₄	Si ₂ *C ₆ H ₁₈ Hg
Si*C ₉ H ₁₄ Mg	Si ₂ *C ₆ H ₁₈ O
Si*C ₉ H ₁₆	Si ₂ *C ₇ H ₁₉ Li
Si*C ₁₁ H ₁₃ Br	Si ₂ *C ₈ H ₂₂ Be
Si*C ₁₁ H ₂₀ AlLi	Si ₂ *C ₈ H ₂₂ BrGa
Si*C ₁₁ H ₂₂	Si ₂ *C ₈ H ₂₂ ClGa
Si*C ₁₂ H ₁₅ B	Si ₂ *C ₈ H ₂₂ ClIn
Si*C ₁₂ H ₂₁ Al	Si ₂ *C ₈ H ₂₂ Hg
Si*C ₁₃ H ₂₇ B	Si ₂ *C ₈ H ₂₂ Mg
Si*C ₁₃ H ₃₃ BN ₂ O ₃	Si ₂ *C ₈ H ₂₄ B ₄
Si*C ₁₄ H ₁₄	Si ₂ *C ₁₀ H ₂₆ MgO
Si*C ₁₄ H ₂₉ BrMgO	Si ₂ *C ₁₁ H ₂₂
Si*C ₁₄ H ₂₉ LiO	Si ₂ *C ₁₂ H ₃₁ B
Si*C ₁₄ H ₄₂ Al ₂ N ₂ P ₂	Si ₂ *C ₁₂ H ₃₄ MgN ₂
Si*C ₁₅ H ₃₆ B ₂	Si ₂ *C ₁₃ H ₃₆ MgN ₂
Si*C ₁₇ H ₁₅ BrMg	Si ₂ *C ₁₄ H ₃₂ BLi
Si*C ₁₇ H ₂₂ BrMg	Si ₂ *C ₁₄ H ₃₄ MgO ₂
Si*C ₁₈ H ₁₅ BrMg	Si ₂ *C ₁₆ H ₂₂ Hg
Si*C ₁₈ H ₁₅ BrMg	Si ₂ *C ₁₆ H ₂₂ Mg
Si*C ₁₈ H ₁₅ Cl	Si ₂ *C ₂₁ H ₂₄
Si*C ₁₈ H ₁₅ K	Si ₂ *C ₃₆ H ₃₀
Si*C ₁₈ H ₁₅ K	Si ₂ *C ₃₆ H ₃₀
Si*C ₁₈ H ₁₅ Li	Si ₂ *C ₃₆ H ₃₀
Si*C ₁₈ H ₁₅ Li	Si ₂ *C ₃₆ H ₃₀ Ba
Si*C ₁₈ H ₁₅ Li	Si ₂ *C ₃₆ H ₃₀ Ca
Si*C ₁₈ H ₁₈ AlLi	Si ₂ *C ₃₈ H ₃₅ Al
Si*C ₁₈ H ₃₈ B ₂	Si ₂ Sr*C ₃₆ H ₃₀
Si*C ₂₁ H ₁₅ CoO ₄	Si ₂ Tl*C ₆ H ₁₈ Cl
Si*C ₂₂ H ₁₅ CoO ₄	Si ₃ *BF ₉
Si*C ₂₂ H ₂₅ Al	Si ₃ *C ₉ H ₂₇ Al
Si*C ₂₂ H ₂₇ BN ₂	Si ₃ *C ₉ H ₂₇ Ga
Si*C ₂₄ H ₂₉ B	Si ₃ *C ₉ H ₂₇ In
Si*C ₂₄ H ₃₀ BN	Si ₃ *C ₉ H ₂₇ N
Si*C ₂₆ H ₃₆ GaP	Si ₃ *C ₉ H ₂₇ P
Si*C ₃₆ H ₃₀ BLi	Si ₃ *C ₁₀ H ₂₇ AlCl ₂
Si*C ₄₀ H ₄₂ BN	Si ₃ *C ₁₀ H ₂₇ Li
Si*ClH ₃	Si ₃ *C ₁₂ H ₃₃ Al
Si*Cl ₂	Si ₃ *C ₁₂ H ₃₃ B
Si*Cl ₂ H ₂	Si ₃ *C ₁₂ H ₃₃ ClMgPb

$\text{Si}_3^* \text{C}_{12} \text{H}_{33} \text{Ga}$	$\text{Sn}^* \text{C}_3 \text{H}_9 \text{BrMg}$
$\text{Si}_3^* \text{C}_{12} \text{H}_{33} \text{In}$	$\text{Sn}^* \text{C}_3 \text{H}_9 \text{Cl}$
$\text{Si}_3^* \text{C}_{12} \text{H}_{33} \text{In}$	$\text{Sn}^* \text{C}_3 \text{H}_9 \text{Li}$
$\text{Si}_3^* \text{C}_{12} \text{H}_{34} \text{Ge}$	$\text{Sn}^* \text{C}_3 \text{H}_9 \text{Li}$
$\text{Si}_3^* \text{C}_{13} \text{H}_{35} \text{AlO}$	$\text{Sn}^* \text{C}_3 \text{H}_{12} \text{BLi}$
$\text{Si}_3^* \text{C}_{13} \text{H}_{35} \text{AlO}$	$\text{Sn}^* \text{C}_3 \text{H}_{17} \text{B}_5$
$\text{Si}_3^* \text{C}_{13} \text{H}_{35} \text{GaO}$	$\text{Sn}^* \text{C}_4 \text{H}_9 \text{N}$
$\text{Si}_3^* \text{C}_{13} \text{H}_{37} \text{AlO}$	$\text{Sn}^* \text{C}_4 \text{H}_{10} \text{AlClF}_2$
$\text{Si}_3^* \text{C}_{15} \text{H}_{39} \text{Al}$	$\text{Sn}^* \text{C}_4 \text{H}_{10} \text{B}_4$
$\text{Si}_3^* \text{C}_{54} \text{H}_{45} \text{Al}$	$\text{Sn}^* \text{C}_4 \text{H}_{12}$
$\text{Si}_3^* \text{C}_{54} \text{H}_{45} \text{AlClK}$	$\text{Sn}^* \text{C}_4 \text{H}_{12}$
$\text{Si}_3^* \text{C}_{72} \text{H}_{60} \text{B}_3 \text{N}_3$	$\text{Sn}^* \text{C}_4 \text{H}_{12} \text{Cl}_3 \text{Ga}$
$\text{Si}_3 \text{Sn}^* \text{C}_{12} \text{H}_{34}$	$\text{Sn}^* \text{C}_4 \text{H}_{12} \text{N}_2$
$\text{Si}_3 \text{Ti}^* \text{C}_9 \text{H}_{27}$	$\text{Sn}^* \text{C}_5 \text{H}_{16} \text{B}_4$
$\text{Si}_3 \text{Ti}^* \text{C}_9 \text{H}_{27}$	$\text{Sn}^* \text{C}_6 \text{H}_6 \text{F}_6$
$\text{Si}_3 \text{Ti}^* \text{C}_{18} \text{H}_{45}$	$\text{Sn}^* \text{C}_6 \text{H}_{15} \text{BN}_2$
$\text{Si}_4^* \text{BF}_{11}$	$\text{Sn}^* \text{C}_6 \text{H}_{15} \text{Li}$
$\text{Si}_4^* \text{C}_4 \text{H}_{12} \text{Cl}_4 \text{O}_4$	$\text{Sn}^* \text{C}_6 \text{H}_{16}$
$\text{Si}_4^* \text{C}_8 \text{H}_{24} \text{O}_4$	$\text{Sn}^* \text{C}_6 \text{H}_{16}$
$\text{Si}_4^* \text{C}_{12} \text{H}_{36} \text{AlK}$	$\text{Sn}^* \text{C}_6 \text{H}_{18} \text{AlLi}$
$\text{Si}_4^* \text{C}_{12} \text{H}_{36} \text{AlLi}$	$\text{Sn}^* \text{C}_6 \text{H}_{18} \text{GaLi}$
$\text{Si}_4^* \text{C}_{12} \text{H}_{36} \text{AlNa}$	$\text{Sn}^* \text{C}_6 \text{H}_{18} \text{InLi}$
$\text{Si}_4^* \text{C}_{12} \text{H}_{36} \text{AlNa}$	$\text{Sn}^* \text{C}_7 \text{H}_{19} \text{Al}$
$\text{Si}_4^* \text{C}_{12} \text{H}_{36} \text{BLi}$	$\text{Sn}^* \text{C}_7 \text{H}_{19} \text{BCIN}$
$\text{Si}_4^* \text{C}_{14} \text{H}_{38} \text{AlCl}$	$\text{Sn}^* \text{C}_8 \text{H}_{12}$
$\text{Si}_4^* \text{C}_{18} \text{H}_{48} \text{AlClO}$	$\text{Sn}^* \text{C}_8 \text{H}_{12} \text{B}_8 \text{Fe}$
$\text{Si}_4^* \text{C}_{24} \text{H}_{66} \text{AlKO}_3$	$\text{Sn}^* \text{C}_8 \text{H}_{16} \text{Si}$
$\text{Si}_4^* \text{C}_{24} \text{H}_{66} \text{AlLiO}_3$	$\text{Sn}^* \text{C}_8 \text{H}_{20}$
$\text{Si}_4^* \text{C}_{24} \text{H}_{66} \text{GaLiO}_3$	$\text{Sn}^* \text{C}_{10} \text{H}_{10}$
$\text{Si}_4^* \text{C}_{26} \text{H}_{52} \text{AlNa}$	$\text{Sn}^* \text{C}_{11} \text{H}_{29} \text{BN}_2$
$\text{Si}_4^* \text{C}_{28} \text{H}_{78} \text{AlLiO}_4$	$\text{Sn}^* \text{C}_{12} \text{H}_{10}$
$\text{Si}_4^* \text{C}_{44} \text{H}_{116} \text{AlNaO}_8$	$\text{Sn}^* \text{C}_{12} \text{H}_{14}$
$\text{Si}_4^* \text{C}_{48} \text{H}_{40} \text{Li}_2$	$\text{Sn}^* \text{C}_{12} \text{H}_{20}$
$\text{Si}_4^* \text{C}_{50} \text{H}_{46} \text{BN}$	$\text{Sn}^* \text{C}_{12} \text{H}_{23} \text{B}_{10}$
$\text{Si}_5^* \text{BF}_{13}$	$\text{Sn}^* \text{C}_{12} \text{H}_{27} \text{ClMg}$
$\text{Si}_6^* \text{C}_{18} \text{H}_{54} \text{AlP}$	$\text{Sn}^* \text{C}_{12} \text{H}_{27} \text{Li}$
$\text{Si}_6^* \text{C}_{21} \text{H}_{57} \text{Ga}$	$\text{Sn}^* \text{C}_{12} \text{H}_{28}$
$\text{Si}_6^* \text{C}_{21} \text{H}_{57} \text{In}$	$\text{Sn}^* \text{C}_{12} \text{H}_{34} \text{Si}_3$
$\text{Si}_6^* \text{C}_{24} \text{H}_{70} \text{Al}_2 \text{N}_2$	$\text{Sn}^* \text{C}_{15} \text{H}_{36} \text{AlLi}$
$\text{Si}_9 \text{Sn}_3 \text{Ti}^* \text{C}_{36} \text{H}_{99}$	$\text{Sn}^* \text{C}_{16} \text{H}_{10} \text{B}_4 \text{Co}_2$
$\text{Si}_9 \text{Ti}^* \text{C}_{36} \text{H}_{99} \text{Ge}_3$	$\text{Sn}^* \text{C}_{16} \text{H}_{12} \text{S}_4$
Sn	$\text{Sn}^* \text{C}_{16} \text{H}_{15} \text{BrMg}$
Sn	$\text{Sn}^* \text{C}_{16} \text{H}_{37} \text{Al}$
Reaction with Be, Mg, Ca, Sr and Ba	$\text{Sn}^* \text{C}_{18} \text{H}_{15} \text{BrMg}$
metals: 5.4.6.1	$\text{Sn}^* \text{C}_{18} \text{H}_{15} \text{Cl}$
$\text{Sn}^* \text{Ba}$	$\text{Sn}^* \text{C}_{18} \text{H}_{16}$
$\text{Sn}^* \text{Ba}_2$	$\text{Sn}^* \text{C}_{18} \text{H}_{19} \text{BrMg}$
$\text{Sn}^* \text{C}_2 \text{H}_6 \text{B}_3$	$\text{Sn}^* \text{C}_{18} \text{H}_{42} \text{AlLi}$
$\text{Sn}^* \text{C}_2 \text{H}_6 \text{Cl}_2$	$\text{Sn}^* \text{C}_{22} \text{H}_{28}$
$\text{Sn}^* \text{C}_2 \text{H}_{11} \text{B}_9$	$\text{Sn}^* \text{C}_{24} \text{H}_{20}$
$\text{Sn}^* \text{C}_2 \text{H}_{18} \text{B}_{10}$	$\text{Sn}^* \text{C}_{24} \text{H}_{20}$
$\text{Sn}^* \text{C}_3 \text{H}_9 \text{Br}$	$\text{Sn}^* \text{C}_{24} \text{H}_{20} \text{AsCl}_3$

$\text{Sn}^*\text{C}_{24}\text{H}_{30}\text{BrMgN}$

$\text{Sn}^*\text{C}_{26}\text{H}_{26}\text{B}_2$

$\text{Sn}^*\text{C}_{48}\text{H}_{40}\text{B}_4$

$\text{Sn}^*\text{C}_{81}\text{H}_{81}\text{BBr}_2\text{P}_6$

$\text{Sn}^*\text{C}_{105}\text{H}_{99}\text{B}_2\text{Br}_2\text{P}_8$

Sn^*Ca

Sn^*Ca_2

Sn^*Cl_2

Sn^*Cl_2

Sn^*Cl_4

Sn^*F_2

Sn^*Mg

Sn^*Mg_2

SnSr

SrSn

Formation: 5.4.6.1

SnSr₂

Sr_2Sn

Formation: 5.4.6.1

$\text{SnTi}^*\text{C}_6\text{H}_{18}\text{Li}$

$\text{SnTi}^*\text{C}_8\text{H}_{21}$

$\text{SnTi}^*\text{C}_{20}\text{H}_{21}$

$\text{Sn}_2^*\text{C}_6\text{H}_{18}$

$\text{Sn}_2^*\text{C}_6\text{H}_{18}$

$\text{Sn}_2^*\text{C}_6\text{H}_{18}$

$\text{Sn}_2^*\text{C}_6\text{H}_{18}\text{Hg}$

$\text{Sn}_2^*\text{C}_{10}\text{H}_{28}\text{BN}$

$\text{Sn}_2^*\text{C}_{10}\text{H}_{30}\text{B}_2\text{N}_2$

$\text{Sn}_2^*\text{C}_{12}\text{H}_{22}$

$\text{Sn}_2^*\text{C}_{12}\text{H}_{30}$

$\text{Sn}_2^*\text{C}_{18}\text{H}_{42}$

$\text{Sn}_2^*\text{C}_{24}\text{H}_{54}$

$\text{Sn}_2^*\text{C}_{36}\text{H}_{30}$

$\text{Sn}_2^*\text{C}_{36}\text{H}_{30}\text{Br}_2\text{Mg}_2$

$\text{Sn}_2^*\text{C}_{36}\text{H}_{30}\text{Mg}$

$\text{Sn}_2^*\text{C}_{36}\text{H}_{30}\text{Mg}$

$\text{Sn}_2\text{Sr}_3^*\text{Al}_2$

$\text{Sn}_2\text{Ti}^*\text{C}_8\text{H}_{24}\text{Li}$

Sn_3^*BaPd

Sn_3^*Ba_5

$\text{Sn}_3^*\text{C}_{13}\text{H}_{35}\text{AlO}$

Sn_3^*Ca

Sn₃Sr

SrSn_3

Formation: 5.4.6.1

Sn₃Sr₅

Sr_5Sn_3

Formation: 5.4.6.1

$\text{Sn}_3\text{Ti}^*\text{C}_{10}\text{H}_{30}\text{Li}$

$\text{Sn}_3\text{Ti}^*\text{C}_{18}\text{H}_{45}$

$\text{Sn}_3\text{Ti}^*\text{C}_{36}\text{H}_{99}\text{Si}_9$

Sn₄Sr

SrSn_4

Formation: 5.4.6.1

$\text{Sn}_4\text{Ti}^*\text{C}_{12}\text{H}_{36}\text{Li}$

Sn_5^*Ba

Sn₅Sr

SrSn_5

Formation: 5.4.6.1

Sr

Sr

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Reaction with R_6Si_2 : 5.4.4.6

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$\text{Sr}^*\text{C}_2\text{H}_6$

$\text{Sr}^*\text{C}_4\text{H}_3\text{IS}$

$\text{Sr}^*\text{C}_4\text{H}_{10}\text{O}_2$

$\text{Sr}^*\text{C}_6\text{H}_5\text{I}$

$\text{Sr}^*\text{C}_7\text{H}_7\text{I}$

$\text{Sr}^*\text{C}_8\text{H}_{20}\text{Al}$

$\text{Sr}^*\text{C}_8\text{H}_{20}\text{B}$

$\text{Sr}^*\text{C}_9\text{H}_{19}\text{IO}_2$

$\text{Sr}^*\text{C}_{10}\text{H}_7\text{I}$

$\text{Sr}^*\text{C}_{10}\text{H}_{21}\text{IO}_2$

$\text{Sr}^*\text{C}_{11}\text{H}_{23}\text{IO}_2$

$\text{Sr}^*\text{C}_{12}\text{H}_{25}\text{IO}_2$

$\text{Sr}^*\text{C}_{14}\text{H}_{14}$

$\text{Sr}^*\text{C}_{16}\text{H}_{16}\text{N}$

$\text{Sr}^*\text{C}_{16}\text{H}_{40}\text{Al}_2$

$\text{Sr}^*\text{C}_{26}\text{H}_{18}$

$\text{Sr}^*\text{C}_{28}\text{H}_{24}$

$\text{Sr}^*\text{C}_{36}\text{H}_{30}\text{Ge}_2$

$\text{Sr}^*\text{C}_{36}\text{H}_{30}\text{Si}_2$

$\text{Sr}^*\text{C}_{40}\text{H}_{38}\text{Ge}_2\text{O}$

Sr^*H_2

Sr^*H_2

Sr^*Pb

Sr^*Pb_3

Sr^*Sn

Sr^*Sn_3

Sr^*Sn_4

Sr^*Sn_5

$\text{SrZn}^*\text{C}_8\text{H}_{20}$

Sr_2^*Pb

Sr_2^*Pb_3

Sr_2^*Sn

$\text{Sr}_3^*\text{Al}_2\text{Sn}_2$

Sr_3^*Pb_5

Sr_5^*Pb_3

Sr_5^*Pb_4

Sr_5^*Sn_3

$\text{Ti}^*\text{C}_4\text{H}_{10}\text{Cl}_2$
 $\text{Ti}^*\text{C}_5\text{H}_5\text{Cl}_3$
 $\text{Ti}^*\text{C}_6\text{H}_{20}\text{O}_4$
 $\text{Ti}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$
 $\text{Ti}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$
 $\text{Ti}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$
 $\text{Ti}^*\text{C}_{16}\text{H}_{36}\text{O}_4$
 Ti^*Cl_3
 Ti^*Cl_4
 Ti^*Cl_4
 Ti^*Cl_4

Tl

Tl

Formation of highly reactive Tl^* :

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Use as an anode: 5.3.6.2.8

Tl^*Br
 Tl^*Br_3
 Tl^*Br_3
 $\text{Tl}^*\text{C}_2\text{H}_3\text{Cl}_2$
 $\text{Tl}^*\text{C}_2\text{H}_4\text{Cl}_3$
 $\text{Tl}^*\text{C}_2\text{H}_6\text{I}$
 $\text{Tl}^*\text{C}_2\text{H}_7\text{N}_2$
 $\text{Tl}^*\text{C}_3\text{Cl}_9\text{O}_6$
 $\text{Tl}^*\text{C}_3\text{F}_9\text{O}_9\text{S}_3$
 $\text{Tl}^*\text{C}_3\text{H}_5\text{Cl}_2$
 $\text{Tl}^*\text{C}_3\text{H}_9$
 $\text{Tl}^*\text{C}_3\text{H}_9$
 $\text{Tl}^*\text{C}_3\text{H}_9$
 $\text{Tl}^*\text{C}_4\text{H}_6\text{Cl}$
 $\text{Tl}^*\text{C}_4\text{H}_7$
 $\text{Tl}^*\text{C}_4\text{H}_{10}\text{I}$
 $\text{Tl}^*\text{C}_4\text{H}_{12}\text{Li}$
 $\text{Tl}^*\text{C}_5\text{Cl}_5$
 $\text{Tl}^*\text{C}_5\text{D}_5$
 $\text{Tl}^*\text{C}_5\text{HD}_4$
 $\text{Tl}^*\text{C}_5\text{H}_5$
 $\text{Tl}^*\text{C}_5\text{H}_9$
 $\text{Tl}^*\text{C}_5\text{H}_9\text{O}_4$
 $\text{Tl}^*\text{C}_6\text{F}_9\text{O}_6$
 $\text{Tl}^*\text{C}_6\text{F}_9\text{O}_6$
 $\text{Tl}^*\text{C}_6\text{H}_8\text{IN}_2$
 $\text{Tl}^*\text{C}_6\text{H}_9\text{O}_6$

$\text{Tl}^*\text{C}_6\text{H}_{10}\text{Cl}$
 $\text{Tl}^*\text{C}_6\text{H}_{13}\text{O}_2$
 $\text{Tl}^*\text{C}_6\text{H}_{15}$
 $\text{Tl}^*\text{C}_6\text{H}_{15}$
 $\text{Tl}^*\text{C}_6\text{H}_{15}$
 $\text{Tl}^*\text{C}_6\text{H}_{18}\text{ClSi}_2$
 $\text{Tl}^*\text{C}_6\text{H}_{18}\text{LiSn}$
 $\text{Tl}^*\text{C}_7\text{H}_7\text{Cl}_2$
 $\text{Tl}^*\text{C}_7\text{H}_{11}$
 $\text{Tl}^*\text{C}_7\text{H}_{15}\text{O}_2$
 $\text{Tl}^*\text{C}_8\text{F}_{11}\text{O}_6\text{S}_2$
 $\text{Tl}^*\text{C}_8\text{HF}_{10}\text{O}_6\text{S}_2$
 $\text{Tl}^*\text{C}_8\text{H}_2\text{F}_9\text{O}_6\text{S}_2$
 $\text{Tl}^*\text{C}_8\text{H}_9\text{Cl}_2$
 $\text{Tl}^*\text{C}_8\text{H}_{17}\text{O}_2$
 $\text{Tl}^*\text{C}_8\text{H}_{21}\text{Sn}$
 $\text{Tl}^*\text{C}_8\text{H}_{24}\text{LiSn}_2$
 $\text{Tl}^*\text{C}_9\text{H}_3\text{F}_{10}\text{O}_6\text{S}_2$
 $\text{Tl}^*\text{C}_9\text{H}_3\text{F}_{10}\text{O}_7\text{S}_2$
 $\text{Tl}^*\text{C}_9\text{H}_{27}\text{Si}_3$
 $\text{Tl}^*\text{C}_9\text{H}_{27}\text{Si}_3$
 $\text{Tl}^*\text{C}_{10}\text{H}_{11}$
 $\text{Tl}^*\text{C}_{10}\text{H}_{30}\text{LiSn}_3$
 $\text{Tl}^*\text{C}_{11}\text{H}_7\text{F}_6\text{O}_4$
 $\text{Tl}^*\text{C}_{11}\text{H}_{15}\text{F}_6\text{O}_5$
 $\text{Tl}^*\text{C}_{11}\text{H}_{15}\text{O}_2$
 $\text{Tl}^*\text{C}_{11}\text{H}_{21}\text{O}_5$
 $\text{Tl}^*\text{C}_{12}\text{BrF}_{10}$
 $\text{Tl}^*\text{C}_{12}\text{H}_8\text{BCl}_2\text{F}_4$
 $\text{Tl}^*\text{C}_{12}\text{H}_{10}\text{BF}_4$
 $\text{Tl}^*\text{C}_{12}\text{H}_{10}\text{Cl}$
 $\text{Tl}^*\text{C}_{12}\text{H}_{21}\text{O}_6$
 $\text{Tl}^*\text{C}_{13}\text{H}_{27}$
 $\text{Tl}^*\text{C}_{12}\text{H}_{36}\text{LiSn}_4$
 $\text{Tl}^*\text{C}_{13}\text{H}_{12}\text{Cl}$
 $\text{Tl}^*\text{C}_{14}\text{H}_{14}\text{BF}_4$
 $\text{Tl}^*\text{C}_{14}\text{H}_{14}\text{BF}_4\text{O}_2$
 $\text{Tl}^*\text{C}_{15}\text{H}_{15}$
 $\text{Tl}^*\text{C}_{16}\text{H}_{18}\text{BF}_4$
 $\text{Tl}^*\text{C}_{16}\text{H}_{18}\text{BF}_4\text{O}_2$
 $\text{Tl}^*\text{C}_{18}\text{F}_{15}$
 $\text{Tl}^*\text{C}_{18}\text{H}_3\text{F}_{12}$
 $\text{Tl}^*\text{C}_{18}\text{H}_{15}$
 $\text{Tl}^*\text{C}_{18}\text{H}_{45}\text{Ge}_3$
 $\text{Tl}^*\text{C}_{18}\text{H}_{45}\text{Ge}_3$
 $\text{Tl}^*\text{C}_{18}\text{H}_{45}\text{Si}_3$
 $\text{Tl}^*\text{C}_{18}\text{H}_{45}\text{Sn}_3$
 $\text{Tl}^*\text{C}_{20}\text{H}_{21}\text{Sn}$
 $\text{Tl}^*\text{C}_{21}\text{H}_9\text{F}_{12}\text{O}_3$
 $\text{Tl}^*\text{C}_{22}\text{H}_{25}\text{Ge}$
 $\text{Tl}^*\text{C}_{30}\text{H}_{27}\text{Fe}_3$
 $\text{Tl}^*\text{C}_{32}\text{H}_{20}\text{F}_{20}\text{N}$

$\text{Ti}^*\text{C}_{36}\text{H}_{99}\text{Ge}_3\text{Si}_9$	$\text{Zn}^*\text{C}_4\text{H}_{12}\text{Li}_2$
$\text{Ti}^*\text{C}_{36}\text{H}_{99}\text{Si}_9\text{Sn}_3$	$\text{Zn}^*\text{C}_4\text{H}_{12}\text{Mg}$
$\text{Ti}^*\text{C}_{38}\text{H}_5\text{F}_{30}\text{Ge}_2$	$\text{Zn}^*\text{C}_4\text{H}_{12}\text{Mg}$
Ti^*Cl	$\text{Zn}^*\text{C}_8\text{H}_{18}$
Ti^*Cl	$\text{Zn}^*\text{C}_8\text{H}_{20}\text{Ba}$
Ti^*Cl_3	$\text{Zn}^*\text{C}_8\text{H}_{20}\text{Ba}$
Ti^*Cl_3	$\text{Zn}^*\text{C}_8\text{H}_{20}\text{Ca}$
Ti^*Cl_3	$\text{Zn}^*\text{C}_8\text{H}_{20}\text{Sr}$
$\text{Ti}^*\text{Cl}_3\text{O}_{12}$	$\text{Zn}^*\text{C}_{12}\text{H}_{10}$
Ti^*Hg	$\text{Zn}^*\text{C}_{12}\text{H}_{10}$
Ti^*I	Zn^*H_2
$\text{Ti}^*\text{N}_3\text{O}_9$	$\text{Zn}^*\text{H}_4\text{Mg}$
Ti^*Na	$\text{Zn}_2^*\text{C}_6\text{H}_8$
Ti^*Na	$\text{Zn}_2^*\text{H}_5\text{K}$
$\text{Zn}^*\text{C}_2\text{H}_6$	$\text{Zn}_2^*\text{H}_5\text{Na}$
$\text{Zn}^*\text{C}_2\text{H}_7\text{K}$	$\text{Zr}^*\text{C}_5\text{H}_{10}\text{D}_3\text{Cl}$
$\text{Zn}^*\text{C}_2\text{H}_7\text{Li}$	$\text{Zr}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$
$\text{Zn}^*\text{C}_2\text{H}_7\text{Na}$	$\text{Zr}^*\text{C}_{11}\text{H}_{13}\text{Cl}$
$\text{Zn}^*\text{C}_2\text{H}_{10}\text{AlLi}$	$\text{Zr}^*\text{C}_{18}\text{H}_{26}\text{AlCl}$
$\text{Zn}^*\text{C}_4\text{H}_{10}$	Zr^*Cl_4
$\text{Zn}^*\text{C}_4\text{H}_{10}\text{O}_2$	

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This index supplements the compound index and the 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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