
Inorganic Reactions
and Methods

Volume 2

Inorganic Reactions and Methods

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Inorganic Reactions and Methods

Volume 2

**The Formation of the Bond
to Hydrogen (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.

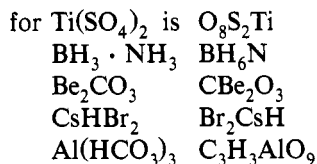
2.5. Author Index

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 re-constructed 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, Alfvén 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

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Inorganic Reactions and Methods, Volume 2

Edited by J.J. Zuckerman, A.P. Hagen

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1. The Formation of Bonds to Hydrogen (Part 2)

1.5. Formation of Bonds between Hydrogen and Elements of Group VB (N, P, As, Sb, Bi)

1.5.1. Introduction

This chapter covers reactions by which bonds between hydrogen and N, P, As, Sb and Bi are formed. A large area of synthetic chemistry is represented, because N—H, and to a lesser extent P—H, bond formation occurs in the context of bio-, organic, organometallic, and inorganic chemistry. Reactions of principal importance to inorganic and organometallic chemists, including those from organophosphorus chemistry, receive major attention. Nitrogen–hydrogen bond formation of principal interest to biological or organic chemistry is presented in less detail.

The group VB element–hydrogen bond formation reactions are presented in broad classes developed according to reagent or reaction type, occasionally requiring arbitrary characterization of systems necessary to allow their classification. Reagents of type X—H are classed as protonic reagents if they participate in reactions as protonic acids, as is the case for molecules in which the electronegativity of X is greater than that of H. Other X—H species are classed as simple hydrides if they contain hydrogen and one element (binary) or hydrogen and two main elements (ternary, e.g., SiH_3PH_2) and as complex hydrides if they contain hydride ions (H^-) coordinated to a central element to form complex anionic species, e.g., LiAlH_4 .

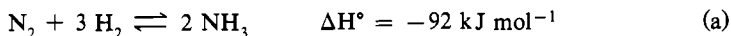
(A.D. NORMAN)

1.5.2. by Reaction of Hydrogen

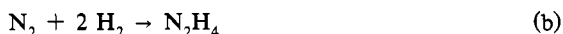
1.5.2.1. with Nitrogen

1.5.2.1.1. from the Elements.

Ammonia is obtained in bulk quantities from the exothermic reaction of gaseous N_2 and H_2 in the well-known process¹:



The equilibrium favors NH_3 formation at low T and high P; e.g., the vol % of NH_3 in a 3:1 H_2 : N_2 mixture are (T and P in parenthesis)²: 14.73 (300°C, 1.01×10^3 Pa), 52.04 (300°C, 1.01×10^4 Pa), 92.55 (300°C, 1.01×10^5 Pa), 57.47 (500°C, 1.01×10^5 Pa). To achieve acceptable reaction rates and conversion to NH_3 , reactions are carried out over an Fe or Fe– Fe_2O_3 catalyst³ at 500°C and ca. 10^5 Pa. Hydrazine forms also in low quantities; too low to provide a useful synthesis¹:



Photolysis of N_2 – H_2 mixtures in the presence of TiO_2 catalyst produces⁴ NH_3 in low yield.

Hydrogen and N_2 react in the presence of $V(OH)_2-Mg(OH)_2$ or $V(OH)_2-ZrO_2$ catalysts in aqueous base to form NH_3 and N_2H_4 . Ammonia production is favored at high catalyst concentration, whereas N_2H_4 is favored at high dilution. Yields of $N_2H_4 \leq 89\%$ are claimed⁵. Hydrogen reacts with N_2 at $50^\circ C$ in H_2O (pH 9–10) containing $Mg^{2+}-Ti(OH)_3-Mo(OH)_3$ catalyst to form⁶ both NH_3 and N_2H_4 .

Atomic nitrogen (4S) reacts with H_2 or H atoms to yield NH_3 and lesser quantities of N_2H_4 ^{7,8}. Reactions in an electrical or microwave discharge, which lead to NH_3 , occur as:



where M is a third body for collisional deactivation.

(A.D. NORMAN)

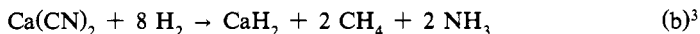
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
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3. A. Ozaki, *Acc. Chem. Res.*, **14**, 16 (1981).
4. G. N. Schrauzer, T. D. Guth, *J. Am. Chem. Soc.*, **100**, 7189 (1978).
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1.5.2.1.2. from Compounds.

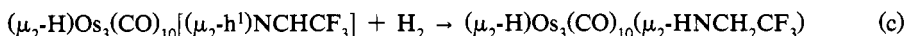
Inorganic nitrogen compounds react with H_2 yielding N–H containing products. Germanium nitride reacts with H_2 at $600^\circ C$:



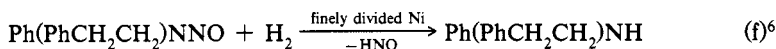
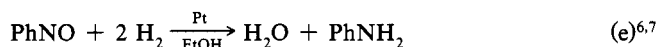
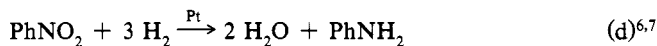
Nitric oxide in H_2O is reduced by H_2 over Pt catalysts to hydroxylamine². Hydrazine in the presence of catalyst is cleaved by H_2 to NH_3 ; however, decomposition of NH_3 to N_2 and H_2 occurs. The N_2 and H_2 are favored at equilibrium except at high T and P. Calcium cyanide reacts with H_2 :



Reaction of an Os-coordinated isocyanate with H_2 (49.5×10^3 Pa) at $140^\circ C$ results in a mixture of products, including those resulting from H_2 addition to the $C \equiv N$ bond⁴:



Hydrogen reduction of organic nitrogen compounds occurs readily in the presence of homogeneous and heterogeneous catalysts,^{5–7} e.g., nitro, nitroso, oxime, nitrile, imine, hydrazone and azide compounds are reduced:



- 4 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.2. by Reaction of Hydrogen
 1.5.2.1. with Nitrogen

Hydrogen and N_2 react in the presence of $V(OH)_2-Mg(OH)_2$ or $V(OH)_2-ZrO_2$ catalysts in aqueous base to form NH_3 and N_2H_4 . Ammonia production is favored at high catalyst concentration, whereas N_2H_4 is favored at high dilution. Yields of N_2H_4 $\leq 89\%$ are claimed⁵. Hydrogen reacts with N_2 at $50^\circ C$ in H_2O (pH 9–10) containing $Mg^{2+}-Ti(OH)_3-Mo(OH)_3$ catalyst to form⁶ both NH_3 and N_2H_4 .

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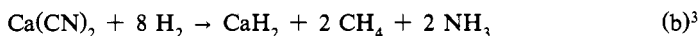
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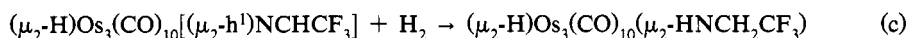
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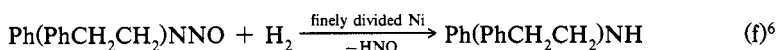
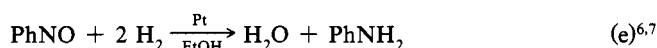
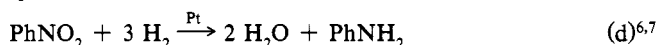
Nitric oxide in H_2O is reduced by H_2 over Pt catalysts to hydroxylamine². Hydrazine in the presence of catalyst is cleaved by H_2 to NH_3 ; however, decomposition of NH_3 to N_2 and H_2 occurs. The N_2 and H_2 are favored at equilibrium except at high T and P. Calcium cyanide reacts with H_2 :

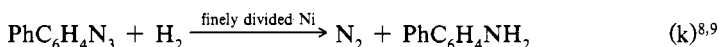
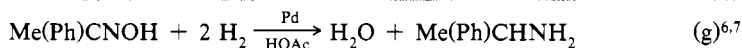


Reaction of an Os-coordinated isocyanate with H_2 (49.5×10^3 Pa) at $140^\circ C$ results in a mixture of products, including those resulting from H_2 addition to the $C \equiv N$ bond⁴:



Hydrogen reduction of organic nitrogen compounds occurs readily in the presence of homogeneous and heterogeneous catalysts,^{5–7} e.g., nitro, nitroso, oxime, nitrile, imine, hydrazone and azide compounds are reduced:





A novel dehydrogenation–reduction of nitrocyclohexane at 420°C over PdO–Al₂O₃ catalysts yields aniline¹⁰:

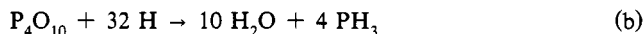


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1.5.2.2. with Phosphorus.

Atomic hydrogen obtained (i) from H₂ dissociation in an electrical discharge, (ii) in a radio-frequency plasma discharge, (iii) photochemically in Hg-sensitized processes, or (iv) at high T reacts with phosphorus or its compounds to form phosphines. Elemental P or P₄O₁₀ and atomic H react^{1,2}:



In the P_(red) reaction, small quantities of P₂H₄ also form. Atomic hydrogen bombardment of InP surfaces generates PH₃ in small quantities³.

Reduction of thio- or selenophosphinic acids by H₂ over finely divided Ni produces phosphine oxides⁴. Reduction of the chiral (R) acids results in inversion of configuration and formation of the (S) oxides⁵:

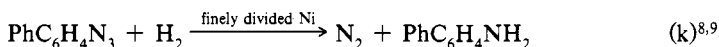
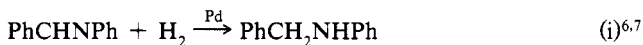
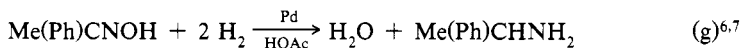


where X = S, Se. Hydrogenolysis of compounds containing activated C—P bonds can result in P—H bond formation⁶:

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi

5

1.5.2. by Reaction of Hydrogen



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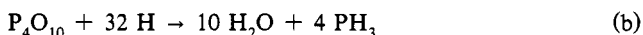


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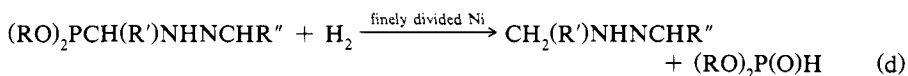


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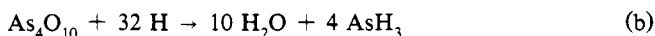
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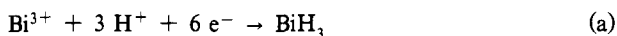


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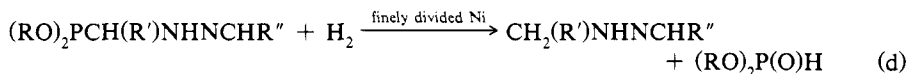


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6 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.2. by Reaction of Hydrogen



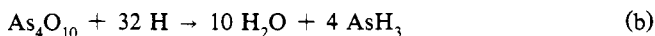
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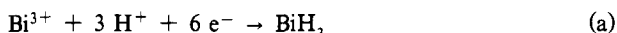


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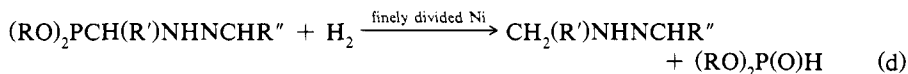


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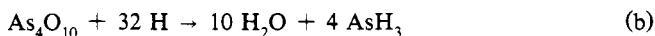
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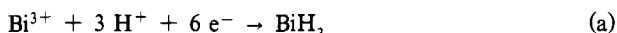


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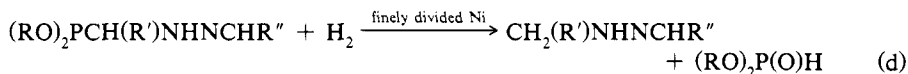


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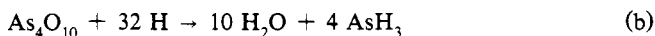
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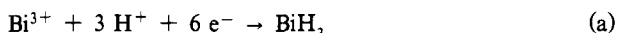


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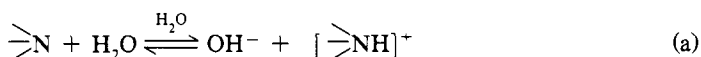
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1.5.3. by Protonation

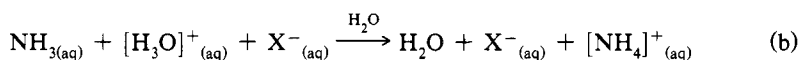
1.5.3.1. of Nitrogen and Nitrogen Compounds

1.5.3.1.1. in Aqueous Systems.

Protonation of amines in H_2O results in N-H bond formation in an equilibrium:

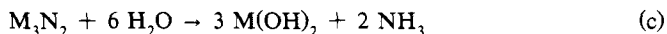


The extent of protonation in pure H_2O depends on temperature and the amine basicity. Equilibrium constants (K_b) for several selected amines at 25°C are^{1,2}: NH_3 , 8.6×10^{-5} ; N_2H_4 , 8.5×10^{-7} ; NH_2OH , 6.6×10^{-9} ; MeNH_2 , 4.5×10^{-4} ; Me_2NH , 5.4×10^{-4} ; PhNH_2 , 4.2×10^{-10} and $\text{C}_5\text{H}_5\text{N}$, 2.3×10^{-9} . For even the strongest bases, e.g., Me_2NH and Et_2NH , at equilibrium in 1 M solutions, < 1% of the amine is present in the protonated (ammonium) form. Addition of protonic acids to aq amine results in further protonation to ammonium species, depending on the acid and concentrations of reacting species^{3,4}:

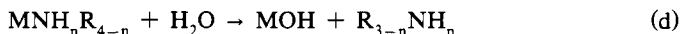


where X^- = e.g., Cl^- , Br^- , $[\text{HSO}_4]^-$.

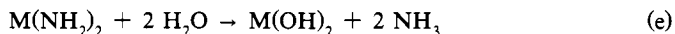
Hydrolysis of ionic nitrides yields^{1,5} NH_3 :



where M = Be, Mg, Ca, Sr, Ba. Replacement of H_2O by D_2O provides^{6,7} a synthesis for ND_3 . Likewise, ionic amides are rapidly converted to amines in high yield^{1,8-10}:

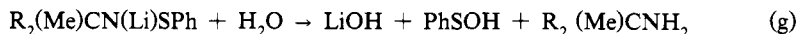
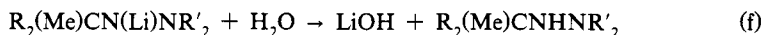


where M = Li, Na, K, Rb, Cs; R = alkyl, aryl, Me_3Si ; n = 0, 1, 2; or:

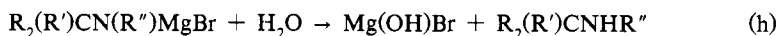


where M = Ca, Ba, Mg, Zn, Cd.

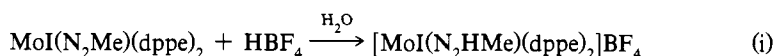
Nitrogen compounds activated or made more basic by metalation or metal coordination undergo protolysis to form N-H bonds. Hydrolyses of Li hydrazide or thioarylamide produce free amines¹⁰:



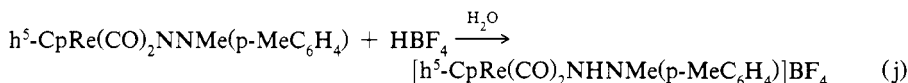
Hydrolysis of magnesium amides from organomagnesium-halide reagent addition to unsaturated nitrogen compounds proceeds similarly^{11,12}:



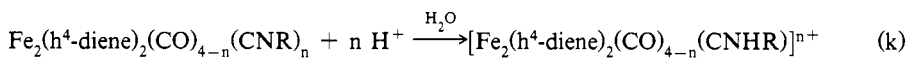
Hydrolysis of the methyl diazenidomolybdenum complex yields the methylhydrazido complex¹³:



where dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. Protonolysis of a disubstituted hydrazidorhenium complex¹⁴:

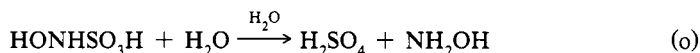
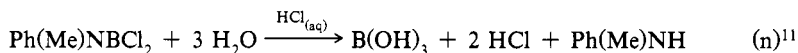
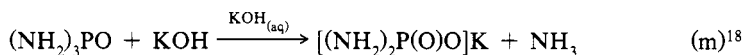
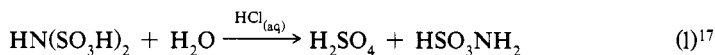


or a coordinated alkylisocyanide¹⁵ yields N—H bond-containing products:

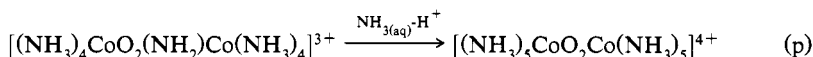


where R = alkyl; n = 1, 2; diene = C₅H₅. Reaction of N₂ with TiCl₃ or VCl₂ and Mg in aq THF, followed by CO₂, produces the complexes MMg₂Cl₂(NCO)(O)(THF)₃ (M = Ti or V), which when hydrolyzed produces¹⁶ CO and NH₃.

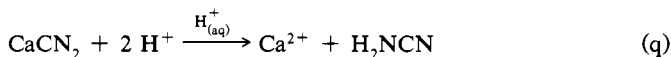
Covalently bonded inorganic amides hydrolyze easily to amines:



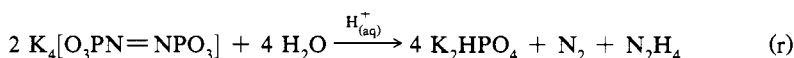
Amido transition-metal complexes are hydrolyzed similarly¹⁰. Complex species, such as the amido-bridged dicobalt complex, undergo reversible hydrolysis in aq acid¹⁹:



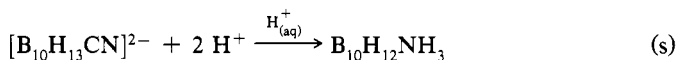
Calcium cyanamide:



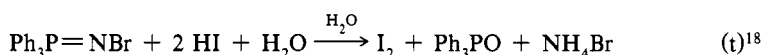
and azodiphosphate:



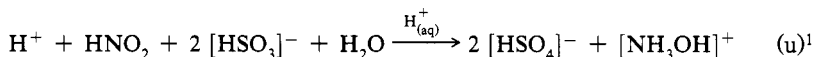
hydrolyses produce H₂NCN¹ and N₂H₄¹⁸, respectively. Passage of [B₁₀H₁₃CN]²⁻ through an acidic ion-exchange column yields the N—H-containing product¹⁹:



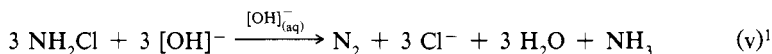
Aqueous reductions are useful for amine synthesis. Organic reducing agents (N₂H₄ or formic acid) reduce amides or imines^{2,9}. Active metals in acid reduce nitro groups^{2,9}. Reduction of Ph₃PNBr with I⁻:



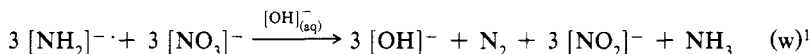
or HNO₂ with [HSO₃]⁻ produces [NH₄]⁺ or [NH₃OH]⁺, respectively:



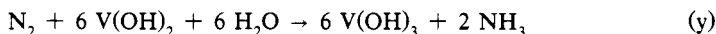
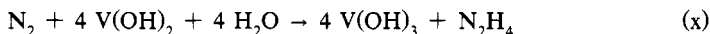
Chloramine:



or $[\text{NH}_2]^- - [\text{NO}_3]^-$ soln reactions yield¹ NH_3 :

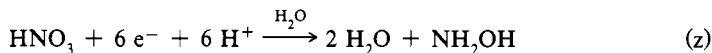


Reduction of dinitrogen to N—H bond products (N_2 fixation) occurs in H_2O -containing inorganic catalysts and reducing agents, perhaps not unlike the biological enzyme nitrogenase^{16,19,20}. Basic solutions (pH = 9–10) containing initially Ti(III), Cr(II) or Zn as reducing agents along with V(II) and Mo(V) species and Mg^{2+} ions react with N_2 to form NH_3 and/or N_2H_4 . The primary reactions are V(II) reductions of N_2 :

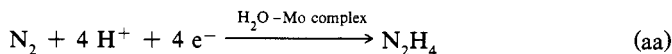


Vanadium(III) reduction by the reducing agent present (e.g., Zn)²⁰ regenerates the necessary V(II) species.

Electrolytic reduction of HNO_3 in aq HCl or H_2SO_4 at Pb electrodes produces NH_2OH in 69% yield¹:



Low yields of N_2H_4 are obtained from N_2 reduction at a Hg cathode in the presence of Mo complexes¹⁶. Electrolysis of N_2 at 40 V for 11 days at a Ni—Cr cathode in (i-PrO)₄Ti—(i-PrO)₃Al solvent, followed by hydrolysis produces low yields²¹ of NH_3 :



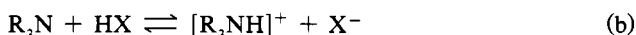
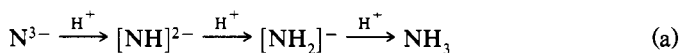
(A.D. NORMAN)

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5. D. T. Hurd, *Chemistry of the Hydrides*, Wiley, New York, 1952.
6. G. Brauer, in *Handbook of Preparative Inorganic Chemistry*, 2nd ed., Vol. 1, G. Brauer, ed., Academic Press, New York, 1963, p. 137.
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12. C. A. Buehler, D. E. Pearson, *Survey of Organic Syntheses*, Vol. 2, Wiley-Interscience, New York, 1977.
13. D. C. Busby, T. A. George, S. D. A. Iske, Jr., S. W. Wagner, *Inorg. Chem.*, **20**, 22 (1981).
14. C. F. Barrientos-Pennos, F. W. B. Einstein, T. Jones, D. Sutton, *Inorg. Chem.*, **21**, 2578 (1982).
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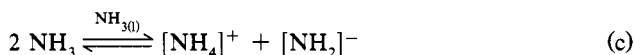
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1.5.3.1.2. in Other Protonic Solvents.

Protonation of nitrogen compounds possessing a lone pair of electrons in a sufficiently acidic solvent yields N—H bonds. Ionic species (e.g., N^{3-}) and neutral compounds (e.g., R_3N) react^{1,2}:

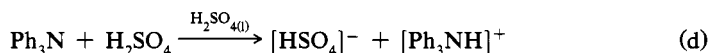


where X = e.g., OR, SR, CO_2Me , OSO_3H , NH_2 , F, Cl, Br or I. The order of relative acidities of common protonic solvent acids is $H_2SO_4 > HX$ (X = halogen) $> RCO_2H > RSH$, $ROH > NH_3$. The order of nitrogen species basicity is $N^{3-} > [RN]^{2-} > [R_2N]^{-} > R_3N$. Treatment of the anions with moderately strong acids (assuming no other reactions at functional R groups), such as ROH, RSH or RCO_2H , yields NH_3 , RNH_2 , or R_2NH , quantitatively^{3,4}. Ammonia dissociates to a small extent:

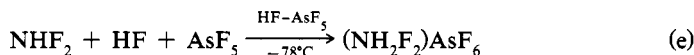


where $K(25^\circ C) = 10^{-27}$ and $K(-50^\circ C) = 10^{-33}$, and substituted amines to a lesser extent form N—H bonds through self-association⁵.

Liquid H_2SO_4 ⁶ and hydrogen halides^{7,8} are acids capable of protonating tricoordinated nitrogen. The order of hydrogen halide acidity is⁸ $HI > HBr > HCl > HF$. Weakly basic amines, e.g., Ph_3N , react with HX ^{7,8} or H_2SO_4 ⁶:

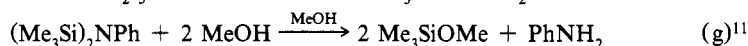
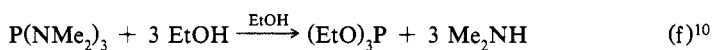


Diffluoramine in $HF-AsF_5$ is protonated⁹ at $-78^\circ C$:



Diffluoramine is potentially explosive and should be handled with care^{5,9}.

Solvolysis of nonmetal amides, through cleavage of the nonmetal–nitrogen bond, can form amines, although these reactions are of interest for the reaction product other than the amine:



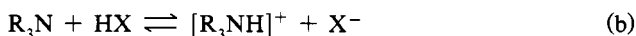
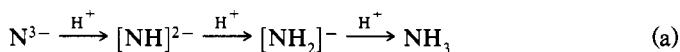
Metal-amide alcoholysis proceeds similarly¹², e.g., the dimethylamidoditungsten complexes react with ROH (R = Me, Et) forming the alkoxide complexes and amine¹³:

10 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
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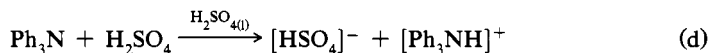


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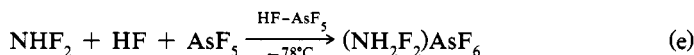


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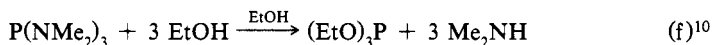


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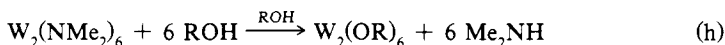


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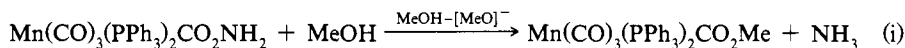
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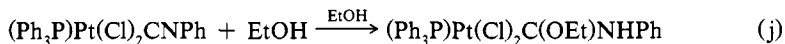
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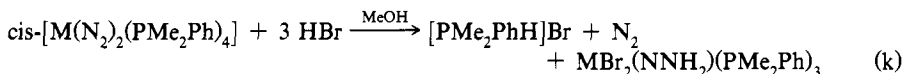
Methanolysis of metal-carbon bonded amides yields¹⁴ NH_3 :



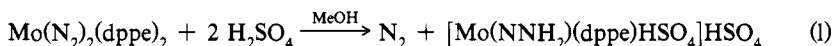
whereas solvolysis of the Pt-coordinated isocyanide produces a coordinated imine¹⁵:



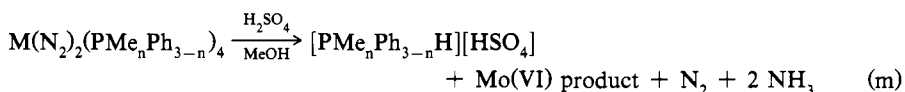
Strong-acid protonation of metal-coordinated N_2 yields products containing $N-H$ bonds. Hydrogen chloride in MeOH reacts with $(h^5-Cp_2Ti)_2N_2MgCl$, forming N_2H_4 in 80% yield¹⁶. Protonation of Mo and W complexes depends on the ligands, the complex geometry, the acid and the reaction conditions¹⁷. The $cis-[M(N_2)_2(PMe_2Ph)_4]$ complexes react with HBr in MeOH to form azenido complexes¹⁷:



where $M = Mo, W$. Similar reactions with H_2SO_4 occur^{2,17}:

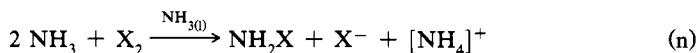


where $dppe = Ph_2PCH_2CH_2PPh_2$, although such reactions proceed further to produce NH_3 and small quantities of N_2H_4 . Ammonia is produced upon strong-acid protonolysis of both cis - and $trans$ - $M(N_2)_2$ (phosphine)₄ complexes:

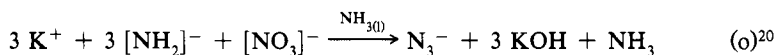


where $M = Mo, W$, and $n = 1, 2$. From the reaction of $trans$ - $W(N_2)_2(PMe_2Ph)_4$ with H_2SO_4 in MeOH or EtOH near quantitative yields of NH_3 arise¹⁷⁻¹⁹. Characterization of the Mo product(s) is better accomplished in nonprotonic solvent systems (see §1.5.3.1.3).

Oxidation of NH_3 in liq NH_3 produces⁵ $[NH_4]^+$:



where $X = Cl, Br, I$. Nitrate oxidation of amide ion yields NH_3 and azide⁵. Hydroxylamine reacts with ClO_3F in EtOH to form $[NH_3OH]^+F^-$, $[NH_3OH][ClO_3]$, O_2 , N_2 and H_2O :



Isolation of products in this reaction presents a potential explosion hazard.

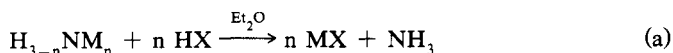
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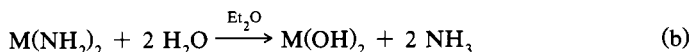
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7. H. H. Hyman, J. J. Katz, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 47.
8. M. E. Peach, T. C. Waddington, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 83.
9. K. O. Christie, *Inorg. Chem.*, **14**, 2821 (1975).
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1.5.3.1.3. with Protonic Acids in Nonprotonic Solvents.

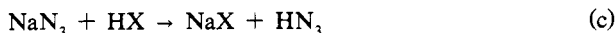
Ionic metal nitrides¹ and amides^{2,3} react with protonic acids (HX):



where M = Li, Na, K, Cs; n = 1, 2, 3; X = Cl, Br, I, HSO₄, H₂PO₄, etc.



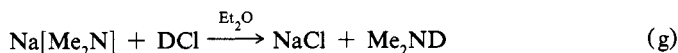
where M = Zn, Cd, Ca, Ba, Sr. Azide², isocyanate², and organic or nonmetal moiety-substituted amides^{3,4} react similarly:



where M = Li, Na, K; R = alkyl, aryl, R₃Si, R₃Ge. Amide ions in the gas phase react with proton sources⁶:



Reactions (a), (b) and (e) are of limited value as routes to N—H bonds because they only regenerate the amine from which the amide is prepared. However, they are useful for preparation of deuterated products, e.g.:

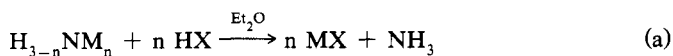


12 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
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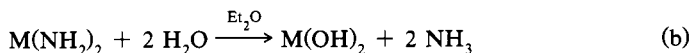
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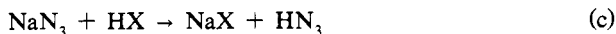
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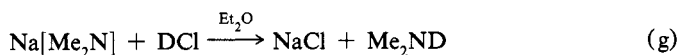
where M = Zn, Cd, Ca, Ba, Sr. Azide², isocyanate², and organic or nonmetal moiety-substituted amides^{3,4} react similarly:

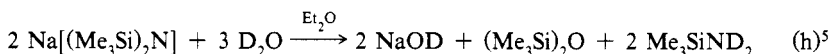


where M = Li, Na, K; R = alkyl, aryl, R₃Si, R₃Ge. Amide ions in the gas phase react with proton sources⁶:



Reactions (a), (b) and (e) are of limited value as routes to N—H bonds because they only regenerate the amine from which the amide is prepared. However, they are useful for preparation of deuterated products, e.g.:



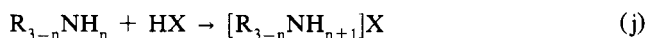


In contrast to ionic phosphides which upon protonolysis yield P_2H_4 along with PH_3 (see §1.5.3.2.1), ionic nitride protonolyses do not yield N_2H_4 , except for Ba_3N_2 which, when heated with H_2O at 380°C , produces⁷ N_2H_4 .

Amines react with protonic acids in nonprotonic solvents or in the gas phase to form ammonium ions. From studies of gas-phase equilibrium reactions between amines and protonic reference acids:

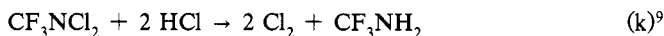


relative basicities of amines, e.g., $\text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{MeNH}_2 > \text{NH}_3$, are known^{8,9}. In solvents the order of relative basicities may differ from that in the gas phase, e.g., $\text{Me}_2\text{NH} > \text{MeNH}_2 > \text{Me}_3\text{N} > \text{NH}_3$ ⁸. Strong acids, such as hydrogen halides, react with amines in nonprotonic solvents:

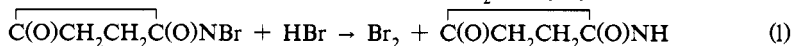


Because the ammonium salts have low solubilities in ether or hydrocarbon solvents, they precipitate, allowing quantitative synthesis^{4,8}.

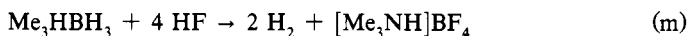
Haloamines react with hydrogen halides in exchange-oxidation and form amine products. Trifluoromethyldichloroamine reacts with HCl at -78°C :



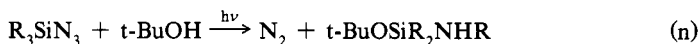
N-Bromosuccinimide with HBr forms succinimide and Br_2 in high yield⁴:



Addition of HF to Me_3NBH_3 produces the tetrafluoroborate-ammonium salt¹⁰:



Addition of HX to unsaturated nitrogen moieties yields amines or ammonium salts. Photolysis of a silylazide in the presence of $t\text{-BuOH}$ yields amine through $t\text{-BuOH}$ reaction with a $\text{R}_2\text{Si}=\text{NR}$ intermediate¹¹:



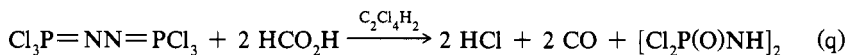
Phosphazenes react with hydrogen halides (HX) to form quaternary salts:



where R = alkyl, aryl; R' = H , alkyl, aryl, SiR_3 , GeR_3 , although HF adds¹⁴ to $(\text{CCl}_3)_2\text{P}(\text{Cl})=\text{NH}$:



and HCO_2H adds¹³ to $(\text{Cl}_3\text{PN})_2$:

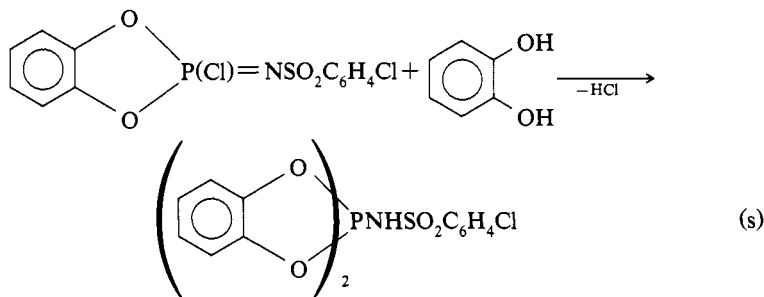


to form aminophosphorus(V) products.

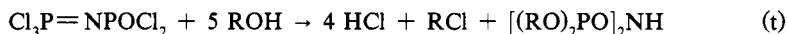
Alcohol addition to the $\text{P}=\text{N}$ bond of a tricoordinated phosphazene occurs:



where $\text{R} = \text{Me}_3\text{Si}$, t-Bu. From reaction of catechol and substituted chlorophosphazene an amidophosphorane is obtained¹⁶:

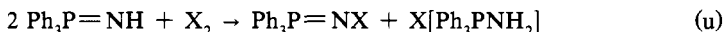


Alcoholysis of the phosphoryl chloride produces the bis(phosphoryl)amine:



where $\text{R} = \text{Me}$, Et, n-Pr.

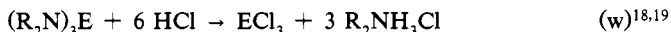
Oxidation of phosphazenes by halogens, interhalogens, or acid chlorides yields amidophosphonium salts¹², e.g.:



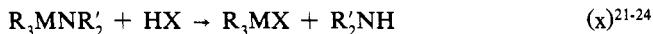
where $\text{X} = \text{Cl}$, Br.

Isocyanates, thioisocyanates, azobenzene and nitriles react with protonic acids to form secondary amines^{4,8}.

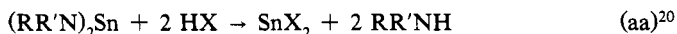
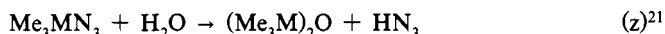
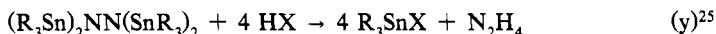
Protonic acid cleavage of compounds containing nonmetal-N or metal-N bonds results in N—H bonds. These reactions produce amines that are more readily prepared by other reactions; hence, they are of limited synthetic utility. Groups IIIB, IVB (except C), and VB (except N) element-N bond cleavage reactions are:



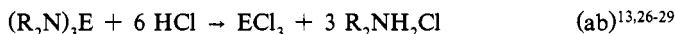
where $\text{E} = \text{B}$, Al, Ga and $\text{R} = \text{alkyl}$, aryl. Group IVB elements, in both 4+ and 2+ oxidation states, are cleaved:



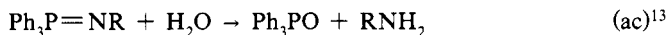
where $\text{M} = \text{Si}$, Ge, Sn, Pb; R and $\text{R}' = \text{alkyl}$, aryl; $\text{X} = \text{Cl}$, Br, I, OH, etc.;



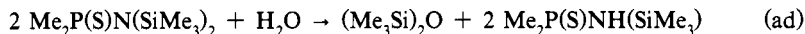
where $\text{R}, \text{R}' = \text{Me}_3\text{Si}$, Me_3Si , Me_3Si , t-Bu; and $\text{X} = \text{Cl}$, MeCO_2 , C_5H_5 . Nitrogen—P, As, or Sb bonds react:



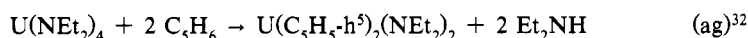
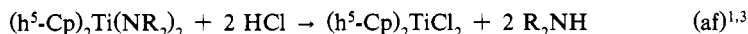
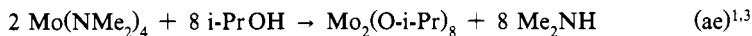
where $\text{E} = \text{P}$, As, Sb; and phosphazenes hydrolyze:



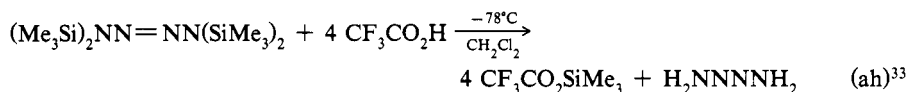
where R = Me, Et, Ph. In a compound containing both Si—N and P—N bonds, H₂O selectively cleaves the Si—N bond³¹:



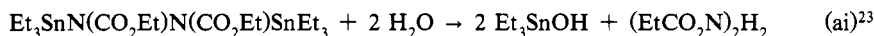
Metal amides react with protonic reagents to produce simple amines:



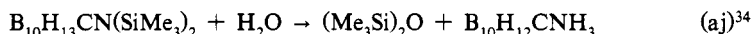
Element (metal or nonmetal)–N protonic acid cleavage yields nitrogen compounds. Reaction of (Me₃Si)₄N₄ with CF₃CO₂H yields N₄H₄:



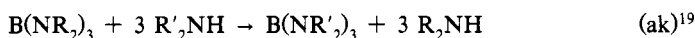
Hydrolyses of the carboxyhydrazide:



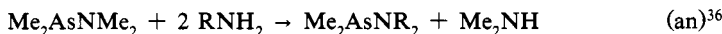
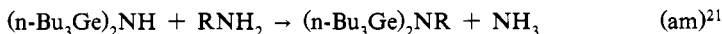
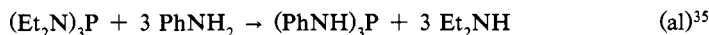
or B₁₀H₁₃CN(SiMe₃)₂ yield novel products:



Transamination, a type of protonic-acid cleavage, yields amine upon exchange with the amide moiety of a nonmetal or metal amide. These reactions are used to prepare amides or imides. The amine formed is of incidental interest, e.g.:

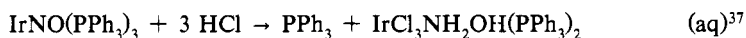
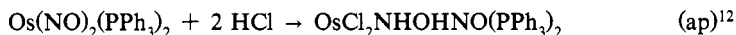
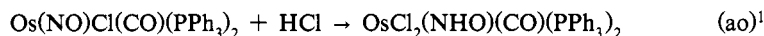


where R, R' = alkyl, aryl, etc.;

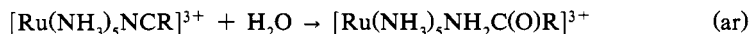


where R = Et, n-Pr, i-Bu. Product formation often requires shifting an equilibrium by removal of the amine formed.

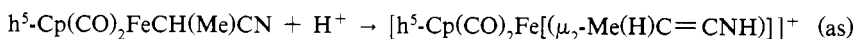
Reactions of transition-metal complex-coordinated ligands with protonic acids can yield N—H bond-containing products. Coordinated nitrosyl groups react with HCl:



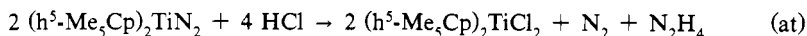
Protonation of an N-coordinated nitrile:



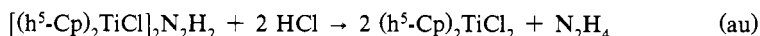
or a cyanoalkyl ion moiety proceed similarly¹:



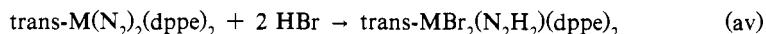
Reactions of dinitrogen (N_2) titanium- or group VIA-(Mo, W) coordinated species with protonic acids can yield N-protonated complexes, or free hydrazines or amines. The $(h^5\text{-Me}_5\text{Cp})_2\text{TiN}_2$ is protonated by HCl to form N_2H_4 in 55% yields³⁸:



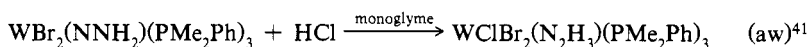
The bis(titanium)hydrazido complex formed by HCl reaction with $(h^5\text{-Cp})_2\text{TiN}_2\text{MgCl}$ in MeOH reacts further with HCl to produce³⁹ N_2H_4 :



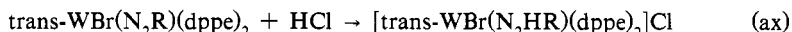
Molybdenum and W complexes undergo protonation to (i) NH intermediates, (ii) NH intermediates which can be further protonated to NH_3 or N_2H_4 , and (iii) N_2H_4 and/or NH_3 directly. $\text{Trans-M}(\text{N}_2)(\text{dppe})_2$ ($\text{M} = \text{Mo}, \text{W}$) reacts with a deficiency⁴⁰ of HBr:



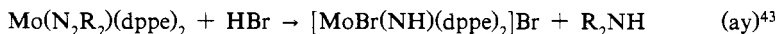
where $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. The WBr_2 complex containing PMe_2Ph ligands, in monoglyme reacts with HCl to form a N_2H_3 complex:



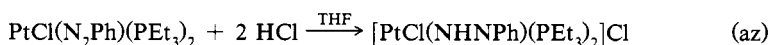
Reactions of metal- N_2R complexes with protonic acids yield hydrazido complexes⁴²:



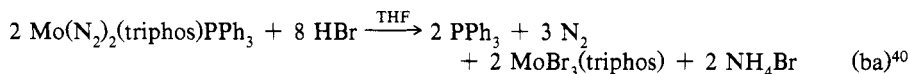
where $\text{R} = \text{Me}, \text{Et}, \text{t-Bu}$, etc. Dialkylhydrazo-Mo complexes are cleaved by HBr:



where $\text{R} = \text{CH}_2(\text{CH}_2)_3\text{CH}_2$. A $\text{Pt-N}_2\text{Ph}$ complex undergoes protonation to the coordinated hydrazido product³⁹:

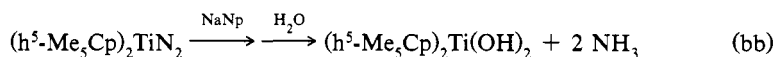


With excess protonic acid, under more vigorous conditions, conversion of N_2 complexes to NH_3 and N_2H_4 occurs. Reaction of $\text{cis-M}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$ ($\text{M} = \text{Mo}, \text{W}$) with x s HCl yields N_2H_4 and NH_3 in ca. 50 and 25 mol % yields⁴⁴. Treatment of these complexes with H_2SO_4 yields NH_3 and N_2 in a 2:1 mol ratio; NH_3 is produced nearly quantitatively:

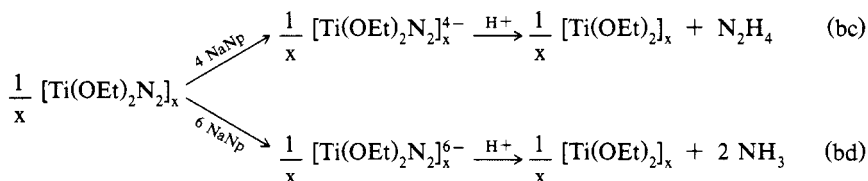


where $\text{triphos} = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$.

Nitrides, formed in N_2 -metal complex reactions, with protonic acids yield N-H bond-containing products. Sodium naphthalide reduction of Et_2TiCl_2 under N_2 in ether⁴⁵ or $(h^5\text{-Me}_5\text{Cp})_2\text{TiN}_2$ in THF³⁹, followed by H_2O treatment, results in 65% conversion of 1 mol of N_2 to NH_3 per mol initial Ti complex:

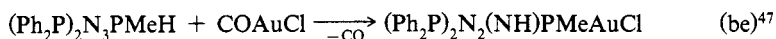


Titanumin ethoxide absorbs N_2 to form a complex that after reduction with 4 or 6 equiv Na naphthalide in THF and treatment with H_2O produces⁴⁵ mainly N_2H_4 or NH_3 :

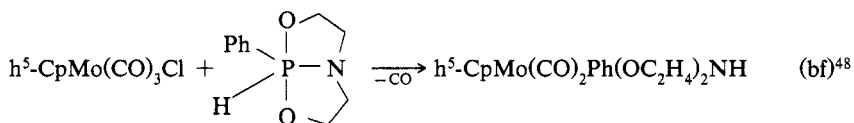


Reaction of $FeCl_3$ with Mg under N_2 yields a complex formulated as $[FeMgCl_3 \cdot (THF)_{1.5}]_2N_2$, which produces N_2H_4 on hydrolysis³⁹. Reaction of $trans-Mo(N_2)_2(dppe)_2$ with a reduced ferredoxin, $[EtSFeS]_4^{3-}$, in monoglyme followed by treatment with HCl yields⁴⁶ NH_3 .

Intramolecular H-exchange reactions, common in organic N-containing molecules, can yield N—H bonds in inorganic or organometallic systems. Metal coordination of the PH phosphazene:



or phosphorane transfers H from P to N:



Structural rearrangement accompanies H-transfer with silylaminophosphines.

(A.D. NORMAN)

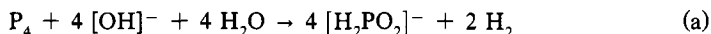
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
3. D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).
4. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961.
5. H. Bürger, *Inorg. Nucl. Chem. Lett.*, **1**, 11 (1965).
6. L. B. Brewster, E. Lee-Ruff, D. K. Bohme, *J. Chem. Soc., Chem. Commun.*, **35** (1973).
7. K.-H. Linke, K. Schroedter, *Z. Anorg. Allg. Chem.*, **413**, 165 (1975).
8. J. R. Malpass, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 3.
9. M. F. A. Dove, D. B. Sowerby, *Coord. Chem. Rev.*, **34**, 262 (1981).
10. J. M. Van Paasschen, R. A. Geanangel, *J. Am. Chem. Soc.*, **94**, 2680 (1972).
11. D. R. Parker, L. H. Sommer, *J. Am. Chem. Soc.*, **98**, 618 (1976).
12. E. W. Abel, S. A. Muckeljohn, *Phosphorus Sulfur*, **9**, 235 (1981).
13. E. Fluck, in *Topics in Phosphorus Chemistry*, M. Grayson, E. J. Griffith, eds., Vol. 4, Wiley-Interscience, New York, 1967, p. 291.
14. E. S. Kozlov, L. G. Dubenko, M. I. Povalotskii, *J. Gen. Chem. USSR (Engl. Transl.)*, **48**, 1734 (1978).
15. O. J. Scherer, N.-T. Kulbach, W. Glässel, *Z. Naturforsch., Teil B*, **33**, 652 (1978).

16. V. P. Kukhar, E. V. Grishkun, V. P. Radovskii, *J. Gen. Chem. USSR (Engl. Transl.)*, **48**, 1308 (1978).
17. L. Riesel, G. Pich, C. Ruby, *Z. Anorg. Allg. Chem.*, **430**, 227 (1977).
18. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
19. K. Niedenzu, J. W. Dawson, *Boron-Nitrogen Compounds*, Academic Press, New York, 1965.
20. D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 895 (1974).
21. F. A. Glockling, *The Chemistry of Germanium*, Academic Press, London, 1969.
22. D. A. Armitage, ed., *Organometallic Chemistry, Specialist Periodical Reports*, Vol. 10, Royal Society of Chemistry, London, 1980, p. 86.
23. J. G. A. Luyten, F. Rykens, G. J. M. Van der Kerk, *Adv. Organomet. Chem.*, **3**, 397 (1965).
24. K. Jones, M. F. Lappert, in *Organotin Compounds*, A. K. Sawyer, ed., Marcel Dekker, New York, 1971, Vol. 2, p. 509.
25. N. Wiberg, M. Veith, *Chem. Ber.*, **104**, 3176 (1971).
26. J. E. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
27. H. R. Allcock, *Phosphorus-Nitrogen Compounds; Cyclic, Linear, and High-Polymeric Systems*, Academic Press, New York, 1972.
28. F. Kober, W. J. Rühl, *Z. Anorg. Allg. Chem.*, **406**, 52 (1974).
29. H. A. Meinemayr, J. G. Noltes, *J. Organomet. Chem.*, **25**, 139 (1970).
30. H. J. Kleiner, *Justus Leibigs Ann. Chem.*, 751 (1974).
31. J. C. Wilburn, R. H. Neilson, *Inorg. Chem.*, **16**, 2519 (1977).
32. T. Marks, *Prog. Inorg. Chem.*, **25**, 223 (1979).
33. N. Wiberg, H. Bayer, H. Bachlihuber, *Angew. Chem., Int. Ed. Engl.*, **14**, 177 (1975).
34. F. R. Scholer, L. J. Todd, *J. Organomet. Chem.*, **14**, 261 (1968).
35. A. Tarassoli, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.*, **21**, 2684 (1982).
36. F. Kober, *Z. Anorg. Allg. Chem.*, **400**, 285 (1973).
37. J. A. McCleverty, *Chem. Rev.*, **79**, 1 (1979).
38. J. E. Bercaw, *J. Am. Chem. Soc.*, **96**, 5087 (1974).
39. J. Chatt, J. R. Dilworth, R. L. Richards, *Chem. Rev.*, **78**, 589 (1978).
40. J. A. Baumann, T. A. George, *J. Am. Chem. Soc.*, **102**, 6153 (1980).
41. T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, *J. Am. Chem. Soc.*, **101**, 3405 (1979).
43. W. Hussain, G. J. Leigh, C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 747 (1982).
44. T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, *J. Am. Chem. Soc.*, **102**, 7461 (1980).
45. E. E. Van Tamelen, *Acc. Chem. Res.*, **3**, 360 (1970).
46. E. E. Van Tamelen, J. A. Gladysz, C. D. Brûlet, *J. Am. Chem. Soc.*, **96**, 3020 (1974).
47. K. C. Dash, A. Schmidpeter, H. Schmidbaur, *Z. Naturforsch., Teil B*, **35**, 1286 (1980).
48. J. Wachler, F. Jeanneaux, J. G. Riess, *Inorg. Chem.*, **19**, 2169 (1980).

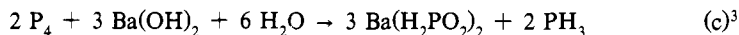
1.5.3.2. of Phosphorus and Phosphorous Compounds

1.5.3.2.1. in Aqueous Systems.

Treatment of P_4 with hot alkali or alkaline-earth hydroxide solutions occurs principally in two ways to form PH_3 and the phosphite and hypophosphite ions¹⁻³:



Disproportionation of P_4 in $Ba(OH)_2$ soln proceeds primarily as:



The $Ba(H_2PO_2)_2$ formed is a major source of the hypophosphite ion and the source of H_3PO_2 which is obtained upon H_2SO_4 acidification of the salt. Moderate yields of PH_3 are reported from reaction⁴ with SeO_2 in H_2O at 19°C:

18 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi

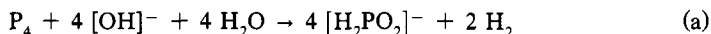
1.5.3. by Protonation

16. V. P. Kukhar, E. V. Grishkun, V. P. Radovskii, *J. Gen. Chem. USSR (Engl. Transl.)*, **48**, 1308 (1978).
17. L. Riesel, G. Pich, C. Ruby, *Z. Anorg. Allg. Chem.*, **430**, 227 (1977).
18. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
19. K. Niedenzu, J. W. Dawson, *Boron-Nitrogen Compounds*, Academic Press, New York, 1965.
20. D. H. Harris, M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 895 (1974).
21. F. A. Glockling, *The Chemistry of Germanium*, Academic Press, London, 1969.
22. D. A. Armitage, ed., *Organometallic Chemistry, Specialist Periodical Reports*, Vol. 10, Royal Society of Chemistry, London, 1980, p. 86.
23. J. G. A. Luyten, F. Rykens, G. J. M. Van der Kerk, *Adv. Organomet. Chem.*, **3**, 397 (1965).
24. K. Jones, M. F. Lappert, in *Organotin Compounds*, A. K. Sawyer, ed., Marcel Dekker, New York, 1971, Vol. 2, p. 509.
25. N. Wiberg, M. Veith, *Chem. Ber.*, **104**, 3176 (1971).
26. J. E. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
27. H. R. Allcock, *Phosphorus-Nitrogen Compounds; Cyclic, Linear, and High-Polymeric Systems*, Academic Press, New York, 1972.
28. F. Kober, W. J. Rühl, *Z. Anorg. Allg. Chem.*, **406**, 52 (1974).
29. H. A. Meinemar, J. G. Noltes, *J. Organomet. Chem.*, **25**, 139 (1970).
30. H. J. Kleiner, *Justus Leibigs Ann. Chem.*, 751 (1974).
31. J. C. Wilburn, R. H. Neilson, *Inorg. Chem.*, **16**, 2519 (1977).
32. T. Marks, *Prog. Inorg. Chem.*, **25**, 223 (1979).
33. N. Wiberg, H. Bayer, H. Bachlihuber, *Angew. Chem., Int. Ed. Engl.*, **14**, 177 (1975).
34. F. R. Scholer, L. J. Todd, *J. Organomet. Chem.*, **14**, 261 (1968).
35. A. Tarassoli, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.*, **21**, 2684 (1982).
36. F. Kober, *Z. Anorg. Allg. Chem.*, **400**, 285 (1973).
37. J. A. McCleverty, *Chem. Rev.*, **79**, 1 (1979).
38. J. E. Bercaw, *J. Am. Chem. Soc.*, **96**, 5087 (1974).
39. J. Chatt, J. R. Dilworth, R. L. Richards, *Chem. Rev.*, **78**, 589 (1978).
40. J. A. Baumann, T. A. George, *J. Am. Chem. Soc.*, **102**, 6153 (1980).
41. T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, *J. Am. Chem. Soc.*, **101**, 3405 (1979).
43. W. Hussain, G. J. Leigh, C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 747 (1982).
44. T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, *J. Am. Chem. Soc.*, **102**, 7461 (1980).
45. E. E. Van Tamelen, *Acc. Chem. Res.*, **3**, 360 (1970).
46. E. E. Van Tamelen, J. A. Gladysz, C. D. Brület, *J. Am. Chem. Soc.*, **96**, 3020 (1974).
47. K. C. Dash, A. Schmidpeter, H. Schmidbaur, *Z. Naturforsch., Teil B*, **35**, 1286 (1980).
48. J. Wachler, F. Jeanneaux, J. G. Riess, *Inorg. Chem.*, **19**, 2169 (1980).

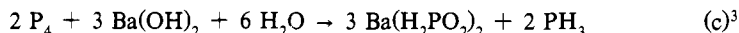
1.5.3.2. of Phosphorus and Phosphorous Compounds

1.5.3.2.1. in Aqueous Systems.

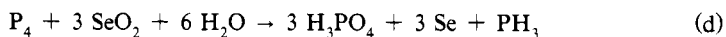
Treatment of P_4 with hot alkali or alkaline-earth hydroxide solutions occurs principally in two ways to form PH_3 and the phosphite and hypophosphite ions¹⁻³:



Disproportionation of P_4 in $Ba(OH)_2$ soln proceeds primarily as:

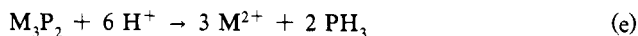


The $Ba(H_2PO_2)_2$ formed is a major source of the hypophosphite ion and the source of H_3PO_2 which is obtained upon H_2SO_4 acidification of the salt. Moderate yields of PH_3 are reported from reaction⁴ with SeO_2 in H_2O at $19^\circ C$:

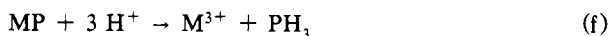


Direct reaction of red phosphorus with $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ at 225–300°C yields PH_3 .

Protonation of -ide salts (e.g., Ca_3P_2 , Mg_3P_2 , Zn_3P_2) in H_2O or strong aq acids yields⁵ PH_3 :



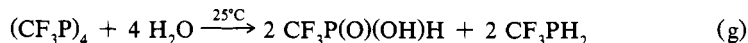
where $\text{M} = \text{Ca}, \text{Mg}, \text{Sr}, \text{Zn}$. From reactions of AIP with H_2SO_4 at -70°C , laboratory quantities of PH_3 (ca. 5 g) can be obtained⁶:



where $\text{M} = \text{Al}, \text{Ga}, \text{In}$. Substantial quantities of P_2H_4 and higher phosphine formation accompanies PH_3 production in Ca_3P_2 hydrolysis. This reaction constitutes the most convenient laboratory synthesis^{3,5,7} of P_2H_4 . Diphosphine is formed directly during hydrolysis, whereas the higher hydrides, e.g., P_nH_{n+2} ($n = 3-9$), P_nH_n ($n = 3-10$), P_nH_{n-2} ($n = 4-12$), etc., result secondarily through P_2H_4 disproportionation (see §1.5.4.2.4).

Small quantities of GeH_3PH_2 or AsH_2PH_2 can be obtained through aqueous acid hydrolysis of ternary alloys or compressed $\text{CaGe}-\text{Ca}_3\text{P}_2$ or $\text{Ca}_3\text{As}_2-\text{Ca}_3\text{P}_2$, respectively⁸. In addition to the ternary hydrides, the expected binary hydrides, e.g., P_2H_4 , GeH_4 , As_2H_4 or P_2H_6 , are obtained.

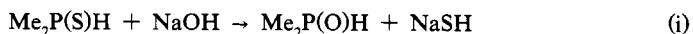
Cleavage of P—P bond-containing compounds, as in the hydrolysis of $(\text{CF}_3\text{P})_4$, yields P—H products⁹. At RT reaction occurs as:



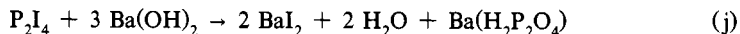
Under more forcing conditions, hydrolysis of the $\text{F}_3\text{C}-\text{P}$ bond occurs to form CF_3H and H_3PO_3 . Tetraalkyldiphosphine disulfides in aqueous base are cleaved:



where $\text{R} = \text{Me}, \text{Et}, n\text{-Bu}$. Although the reaction does not work well when $\text{R} = \text{Ph}$ ¹⁰, excellent yields of $\text{Me}_2\text{P}(\text{S})\text{H}$ are obtained¹¹. Subsequent conversion of this product in NaOH soln to $\text{Me}_2\text{P}(\text{O})\text{H}$ occurs:

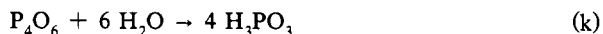


and if conditions are not controlled carefully this hydrolysis product can dominate. Diphosphorus tetraiodide in aq $\text{Ba}(\text{OH})_2$ yields hypodiphosphite as $\text{Ba}(\text{H}_2\text{P}_2\text{O}_4)$ along with a complex mixture of other phosphorus acid materials¹²:

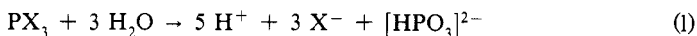


Group IVB (Si, Ge, Sn) element–phosphorous compound hydrolysis in H_2O yields phosphines, although reactions with protonic acids in nonprotic solvents are more useful (see §1.5.3.2.3).

Hydrolyses of P(III) compounds, e.g., P_4O_6 , yields H_3PO_3 quantitatively²:

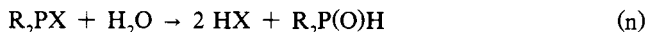


Phosphorus trihalide (PCl_3 , PBr_3 , PI_3) products depend on T, reagent ratios and solution pH^{2,13}. In hydrochloric acid at 25°C , PCl_3 , PBr_3 and PI_3 react primarily as:

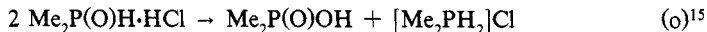


Evaporation of volatiles from $\text{PCl}_3\text{-H}_2\text{O}$ yields crystalline H_3PO_3 quantitatively. Hydrolysis of phosphorus trihalides at 0°C in an NaHCO_3 buffer forms mixtures, including $[\text{HPO}_3]^{2-}$, $[\text{H}_2\text{PO}_3]^-$, $[\text{H}_2\text{PO}_5]^{2-}$, $[\text{P}_2\text{O}_6]^{4-}$, $[\text{PO}_4]^{3-}$, and $[\text{P}_2\text{O}_7]^{4-}$. From the PBr_3 reaction, upon addition of HBr and alcohol, crystalline $\text{Na}_3[\text{HP}_2\text{O}_5] \cdot 12 \text{H}_2\text{O}$ is obtained.

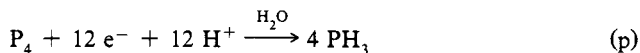
Aqueous acid-solution hydrolysis of R_2PX or RPX_2 species forms phosphine oxides and phosphinic acids, respectively^{2,14}:



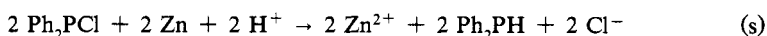
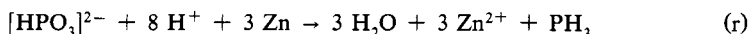
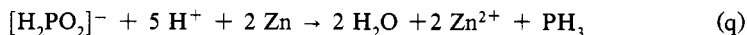
where R = alkyl, aryl; X = halide, alkoxy, aryloxy. The $\text{Me}_2\text{P(O)H}$ can be isolated as a hydrochloride adduct, which at 80°C decomposes as:



Phosphine is formed when P_4 in aqueous acid is treated with Zn amalgam⁵. Electrolysis of H_3PO_3 or H_3PO_2 , at Pd or Hg cathodes, produces^{5,16} some PH_3 :



At black phosphorous¹⁷ or InP cathodes¹⁸, electrolytic reduction of the electrode to PH_3 occurs. Zinc in aqueous acid reduces $[\text{H}_2\text{PO}_4]^-$ or $[\text{HPO}_3]^{2-}$ to PH_3 ¹⁹ and Ph_2PCl to Ph_2PH ²⁰:



(A.D. NORMAN)

1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
3. G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd ed., Vol. 1, Academic Press, New York, 1963.
4. E. Montignie, *Z Anorg. Allg. Chem.*, 306, 235 (1960).
5. E. Fluck, *Top. Curr. Chem.* 35, 3 (1973).
6. R. C. Mariott, J. D. Odom, C. T. Sears, Jr., *Inorg. Synth.*, 14, 1 (1973).
7. M. Baulder, *Angew. Chem., Int. Ed. Engl.*, 21, 492 (1982).
8. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.* 4, 1 (1968).
9. A. H. Cowley, in *Topics in Phosphorus Chemistry*, Vol. 4, M. Grayson, E. J. Griffith, eds., Interscience, New York, 1967, p. 1.
10. L. Maier, *Prog. Inorg. Chem.* 5, 27 (1963).
11. R. A. Malevannaya, E. N. Tsvetkov, M. I. Kabachnik, *Bull. Acad. Sci., USSR Div. Chem. Sci.*, 936 (1976).
12. M. Baudler, M. Mengel, *Z. Anorg. Allg. Chem.*, 374, 159 (1970).
13. D. S. Payne, in *Topics in Phosphorus Chemistry*, Vol. 4, M. Grayson, E. J. Griffith, eds., Interscience, New York, 1967, p. 35.
14. A. W. Frank, *Chem. Rev.*, 61, 389 (1961).
15. H. J. Kleiner, *Justus Liebigs Ann. Chem.*, 751 (1974).
16. V. P. Gladyshev, *Tr. Inst. Khim. Nauk Akad. Nauk, Kaz. SSR*, 35, 74 (1973); *Chem. Abstr.*, 80, 43,447 (1974).

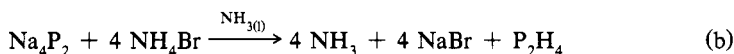
17. I. Chernykh, E. V. Zubova, V. V. Savranskii, A. P. Tomilov, *Sov. Electrochem. (Engl. Transl.)*, 16, 1797 (1980).
 18. G. I. Erusalimchik, D. M. Levin, *Sov. Electrochem. (Engl. Transl.)*, 16, 1854 (1980).
 19. L. Maier, *Prog. Inorg. Chem.*, 5, 27 (1963).
 20. D. T. Burns, A. Townshend, A. H. Carter, in *Inorganic Reaction Chemistry*, Vol. 2, Part B, Ellis Harwood, Chichester, England, 1981, p. 327.

1.5.3.2.2. in Other Protonic Solvents.

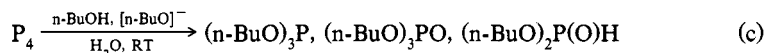
Reactions of alkali-metal phosphides in liq NH_3 with protonic acids, such as NH_4Br , readily yield phosphine or substituted derivatives^{1,2}:



e.g., PH_3 ³ and Ph_2PH_4 are obtained upon protonation of Ph_2PNa and KPH_2 , respectively, in over 80% yield. Similarly, NH_4Br or H_2O protonation of Na_4P_2 in liq NH_3 produces⁵ P_2H_4 :



White phosphorus reacts in $n\text{-BuOH-CCl}_4$ mixed solvent with $[\text{n-BuO}]^-$ to form $(\text{n-BuO})_2\text{P(O)H}$, in yields⁶ $\leq 82\%$:

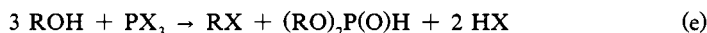


With 2 equiv of $[\text{n-BuO}]^-$, no $(\text{n-BuO})_2\text{P(O)H}$ is obtained.

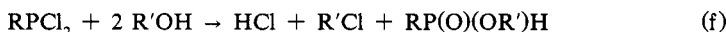
Halophosphorus-(III) species undergo² alcoholysis to alkyl halides and H_3PO_3 :



Under controlled conditions, phosphonate products (e.g., $\text{R} = \text{Me, Et, Ph, C}_6\text{H}_{11}$) can be obtained⁷:

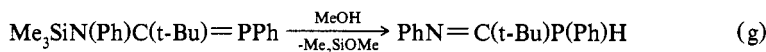


Alkyldichlorophosphines react in alcohol to form phosphinate esters, e.g.:

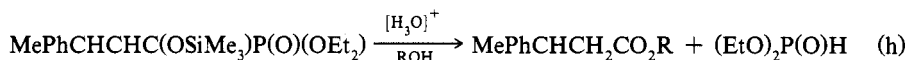


Yields of t-BuP(O)(OEt)H ⁸ and MeP(O)(OR')H ($\text{R}' = \text{Et, n-Pr, i-Bu, n-Bu}$)⁹ $\leq 98\%$ can be obtained.

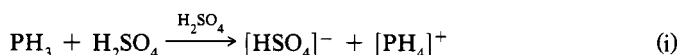
Phosphaethene reacts in refluxing MeOH to form a secondary phosphine:



In contrast, treatment of the vinylphosphonate with alcoholic acid cleaves the phosphoryl moiety with no addition to the vinyl double bond¹⁰:

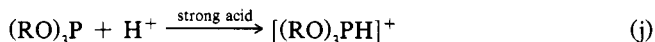


Protonation of phosphine, phosphites or phosphorous halides in strong acid forms P-H bonds. Phosphine in conc H_2SO_4 or HCl is converted^{11,12} to $[\text{PH}_4]^+$:

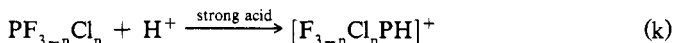


22 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.3. by Protonation
 1.5.3.2. of Phosphorus and Phosphorous Compounds

Protonation of phosphinic acid, phosphites,¹³ or halophosphines¹⁴ by FSO_3H or $\text{FSO}_3\text{H-SbF}_5$ in SO_2 at low T yields phosphonium ions, as observed in ^1H and ^{31}P NMR spectra, e.g.:



where R = H, Me, Et, i-Pr, n-Bu, Ph;



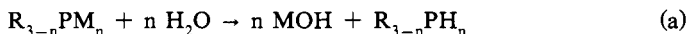
where n = 1–3.

(A.D. NORMAN)

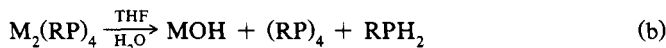
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
3. R. G. Hayter, F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).
4. R. I. Wagner, A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3869 (1953).
5. E. C. Evers, E. H. Street, Jr., S. L. Lung, *J. Am. Chem. Soc.*, **73**, 5088 (1951).
6. C. Brown, R. F. Hudson, G. A. Warten, H. Coates, *Phosphorus Sulfur*, **6**, 481 (1979).
7. D. S. Payne, in *Topics in Phosphorus Chemistry*, M. Grayson, E. J. Griffith, eds., Vol. 4, Wiley-Interscience, New York, 1967, p. 85.
8. D. C. Crofts, D. M. Parker, *J. Chem. Soc., C*, 332 (1970).
9. M. Fink, H. J. Kleiner, *Justus Leibigs Ann. Chem.*, 741 (1974).
10. T. Hata, M. Nakajima, M. Sekine, *Tetrahedron Lett.*, 2047 (1979).
11. M. E. Peach, T. C. Waddington, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 83.
12. R. J. Gillespie, E. A. Robinson, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 117.
13. G. A. Olah, C. W. McFarland, *J. Org. Chem.*, **36**, 1374 (1971).
14. L. J. Vande Griend, J. G. Verkade, *J. Am. Chem. Soc.*, **97**, 5958 (1975).

1.5.3.2.3. with Protonic Acids in Nonprotonic Solvents.

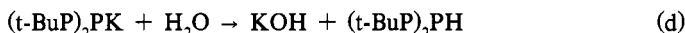
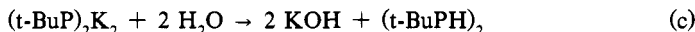
Protonation of phosphides results in direct formation of P—H bonds.^{1,2} Reactions of alkali-metal mono- and disubstituted phosphides with H_2O in ethers leads to:



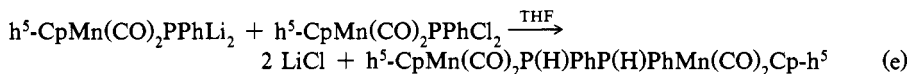
where n = 1, 2, 3; R = alkyl, aryl; M = Li, Na, K; e.g., PH_3 , PhPH_2 , Et_2PH , Ph_2PH , EtPhPH , in 30–80% yields. Metal salts of di- and tetraphosphines react to form phosphines and cyclopolyphosphines³:



where M = Li, K; R = Me, Et, C_6H_{11} . t-Butyl-substituted lithio di- and triphosphines upon hydrolysis generate the parent phosphines^{3,4}:



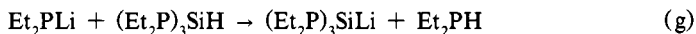
The $\text{h}^5\text{-Cp}(\text{CO})_2\text{Mn}$ -coordinated $(\text{PhPH})_2$ forms in a reaction involving an -ide salt in which protons are abstracted from the THF solvent⁵:



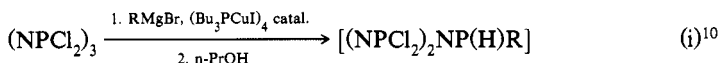
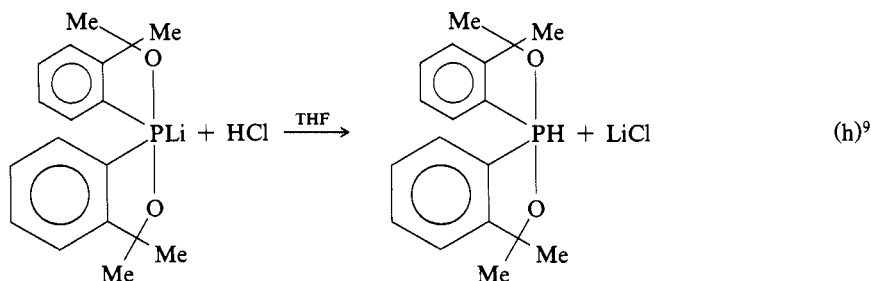
Complex phosphido- or alkylphosphidoaluminates quantitatively hydrolyze to form⁶ PH_3 or primary and secondary phosphines, e.g.:



The strongly basic Et_2PLi deprotonates $(\text{Et}_2\text{P})_3\text{SiH}$:

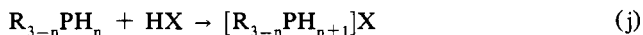


however, no reaction occurs⁸ with $(\text{Et}_2\text{P})_2\text{SiH}_2$. Reaction of HCl with a spiro-phosphorus(V) anion and treatment of the $(\text{NPCl}_2)_3$ alkylmagnesium halide reagent product with $i\text{-PrOH}$ proceed:

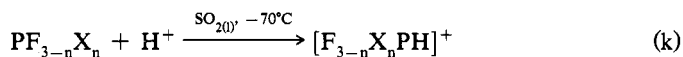


where $\text{R} = \text{Me, Et, } i\text{-Pr, } n\text{-Pr, } n\text{-Bu}$. Deuterium-labeling experiments show the P-H hydrogen comes from the $n\text{-PrOH}$.

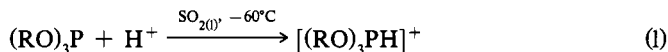
Phosphonium salts containing a P-H bond form in condensed phases upon strong-acid protonation^{1,11} or in the gas phase by hydrogen-ion protonation^{7,12} of phosphines:



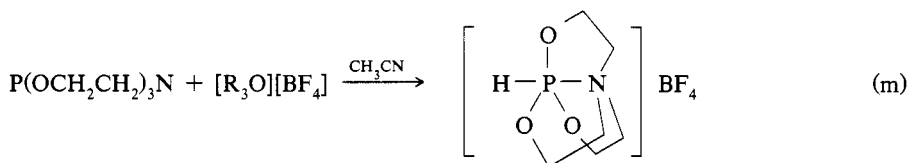
where $\text{R} = \text{H, alkyl, aryl}$; $\text{X} = \text{Cl, Br, I}$ and $n = 0-3$. The more strongly basic alkylphosphines react quantitatively. Phosphonium chloride or bromide is highly dissociated at RT; PH_4I forms a solid stable adduct¹. The perfluoroalkylphosphines are cleaved by HX to CF_3H and the respective P(III) halide. Phosphorus(III) halides and phosphites are protonated in strong acid media, e.g. $\text{HSO}_3\text{F-SbF}_5$ in SO_2 at -60°C to -70°C ¹³:



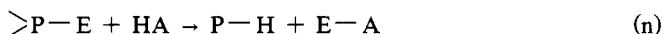
where $\text{X} = \text{Cl, } n = \text{X} = \text{Br, } n = 1-3$;



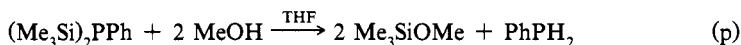
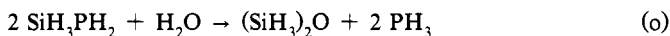
where $\text{R} = \text{Me, Et, } i\text{-Pr, } n\text{-Bu, Ph}$. Tetramethyldiphosphine is protonated¹¹ by HCl in CHCl_3 . Reaction of the P -containing cage, $\text{P}(\text{OCH}_2\text{CH}_2)_3\text{N}$, with $[\text{R}_3\text{O}][\text{BF}_4]$ in CH_3CN gives the intramolecularly P-N -coordinated cage in 80% yield¹⁴:



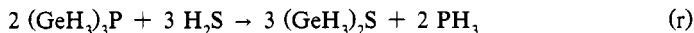
Protonic acid cleavage of bonds between P and group IVB elements (E = Si, Ge, Sn) yields P—H bonds¹⁵⁻¹⁷:



Reactions involving the acids H_2O , H_2S , ROH , RSH , NH_3 , RNH_2 , RCCH , and RCO_2H in the gas phase or in nonprotic solvents, form, e.g., $\text{R}_{3-n}\text{PH}_n$ ($n = 1-3$), PH_3 ¹⁵⁻²⁰, RPH_2 ($\text{R} = \text{Me, Et, t-Bu, Ph}$)^{15,21} and R_2PH ($\text{R} = \text{Me, Et, Ph}$)^{15,16,21,22}:



The order of acid reactivity is hydrogen halides > alcohol, thiols > amines. It is noteworthy that $(\text{GeH}_3)_3\text{P}$ is inert to H_2O cleavage but reacts rapidly¹⁶ with H_2S :



Cleavage of Si—P bonds is fast; Ge—P and Sn—P bonds are less reactive; $\text{Ph}_3\text{SnPPh}_2$ is inert¹⁵ to hot H_2O . The stepwise nature of multiple cleavage reactions can be used to prepare intermediate cleavage products, e.g., under controlled conditions both $\text{Me}_3\text{SiP}(\text{H})\text{Ph}$:

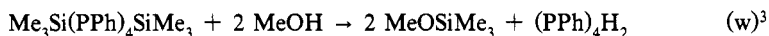
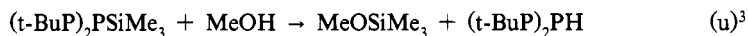


and PhPH_2 :

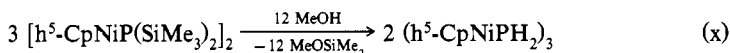


can be obtained²¹ from the alcoholysis of $(\text{Me}_3\text{Si})_2\text{PPh}$.

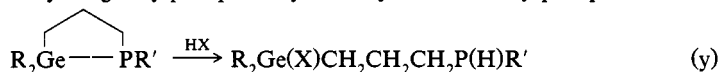
Protonic acid cleavage of group IVB element (Si, Ge)-P bonds is most valuable synthetically to prepare P—H bond-containing higher phosphines or metal complexes:



Methanolysis of silylated metal phosphido complexes yields phosphido complexes,²³ e.g.:



Acid cleavage of the cyclic germylphosphines yields acyclic secondary phosphines²⁴:

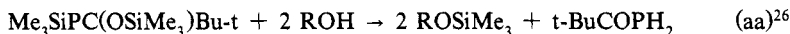


where R = Et, R' = Et, Ph; X = Cl, OH, OMe, SEt, OAc.

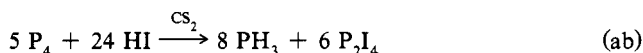
Alcohol cleavage of C—P bonds can form P—H bond-containing products. Methanol cleaves (MeCO)₃P stepwise, forming²⁵ PH₃:



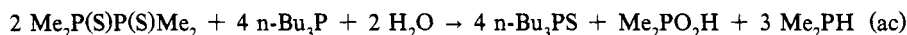
Cleavage of the P=C bond in a phosphathene proceeds:



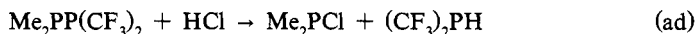
Protonic acid cleavage of the P—P bonds in P₄ yields compounds containing P—H bonds. Reaction at 25°C with HI yields PH₃ and P₂I₄ quantitatively²⁷:



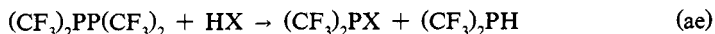
Dimethylphosphine, from H₂O cleavage of Me₂P(S)P(S)Me₂ in the presence of n-Bu₃P at 160–170°C, is obtained in 66% yield²⁸:



This synthesis of Me₂PH is better than the LiAlH₄–Me₂P(S)P(S)Me₂ method described in §1.5.5.2.2. The unsymmetrically substituted diphosphine Me₂PP(CF₃)₂ reacts with HCl:



or H₂O at 25°C, forming (CF₃)₂PH in 98% and 79% yields, respectively²⁹. Dry HI, H₂O, or Me₂AsH and (CF₃)₂PP(CF₃)₂ react:



where X = I, OH, AsMe₂. Ring opening and partial degradation of (CF₃P)₄ by H₂O in diglyme yields a mixture²⁹ of (CF₃P)₂H₂ and (CF₃P)₃H₂. Reduction–scission of Me₄P₂ by RuCl₃·x H₂O forms metal-coordinated³⁰ Me₂PH:

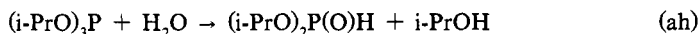


Trimethylstannane cleavage of metal-coordinated diphosphines yields metal-coordinated³¹ (CF₃)₂PH:

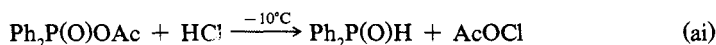


where R = Me, CF₃; M = Cr, Mo.

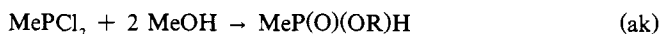
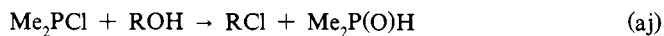
Hydrolysis or alcoholysis of P(III) halides, especially PCl₃ and PBr₃, yields H₃PO₃; however, these reactions are better carried out in H₂O or alcoholic media^{1,7} (see §1.5.3.2.1 and §1.5.3.2.2). Hydrolysis of trialkyl or triarylphosphites occurs readily, e.g., reaction⁷ of (i-PrO)₃P with H₂O in CH₃CN:



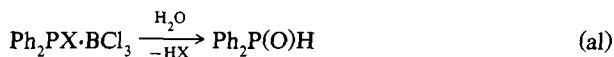
Dry HCl reacts with Ph₂P(O)Ac, yielding Ph₂P(O)H³³:



Controlled reactions of Me₂PCl with H₂O or MeOH and MePCl₂ with MeOH³⁴ yield Me₂P(O)H and MeP(O)HOMe, respectively:

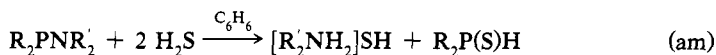


where R = H, Me. Boron-trichloride coordination of tertiary Ph_2PX phosphines, followed by addition of H_2O , produces $\text{Ph}_2\text{P(O)H}$ in 68–87% yield³⁵:

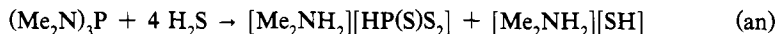


where X = CH_2OMe , CH_2SMe , C(O)Ph . Hydrolysis of cyclic secondary phosphine chlorides results in the cyclic phosphine oxide in high yield³⁶.

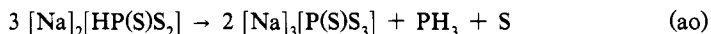
Aminophosphines can react with protonic acids (HX) to form P—H bonds. Generally, such reactions produce NH and PX products, owing to the polarity of the P—N bond^{1,37}. Hydrogen sulfide and dialkylaminodialkylphosphines in benzene at 80°C yield dialkylphosphine sulfides quantitatively³⁷:



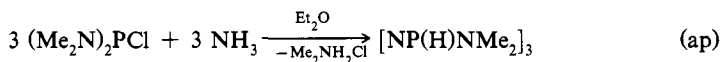
where R = Et; R' = Me, Et, t-Bu, Ph. Tris(dimethylamino)phosphine reacts with H_2S :



Conversion of thiophosphite to its Na salt, followed by thermolysis, yields PH_3 quantitatively³⁸:

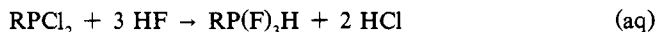


Ammonia and $(\text{Me}_2\text{N})_2\text{PCl}$ in diethyl ether form the hydridocyclophosphazene³⁹:



An aminophosphine intermediate forms, which tautomerizes to the final product.

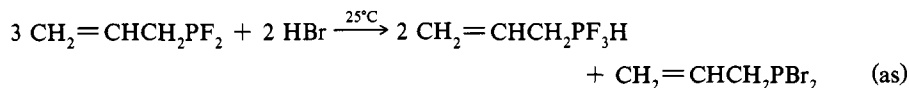
Oxidative addition of protonic acids to P(III) compounds yields P—H-phosphoranes. Alkyldichlorophosphines react at –30 to –20°C with HF in CCl_3 solvent to form equatorially substituted products⁴⁰:



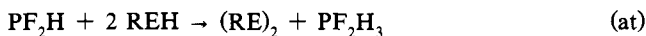
where R = Me, Et, n-Bu, t-Bu, Ph. In the presence of H_2O , the phosphonous acid fluorides forms⁴¹:



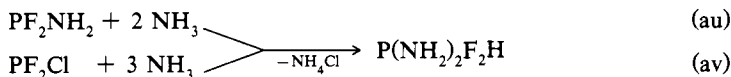
Gaseous HBr and allyldifluorophosphine undergo exchange and addition⁴²:



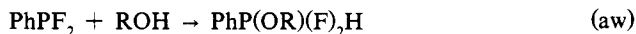
Gaseous NH_3 and PF_2NH_2 or PF_2Cl react⁴³ at 25°C. Alcohols and thiols, with PF_2H at 0°C, form⁴⁴ PH_2F_2 :



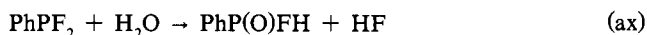
where R = Me, Et; E = O, S;



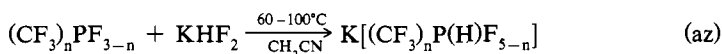
Alcohols react with PhPF_2 in benzene to form P—H-fluorophosphoranes⁴⁵:



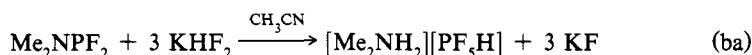
where R = Me, Et, CF_3CH_2 , $(\text{CF}_3)_2\text{CH}$, $\text{Ph}(\text{CF}_3)\text{CH}$, t-Bu, whereas H_2O reacts in a two-step process to produce the final PhPF_3H :



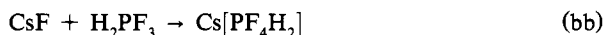
Six-coordinated P—H-phosphoranes form⁴⁶ P(III) compounds and from $[\text{HF}_2]^-$:



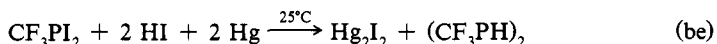
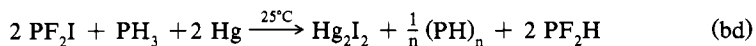
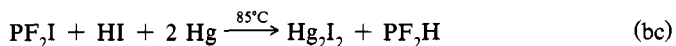
where n = 0,1,2; or from:



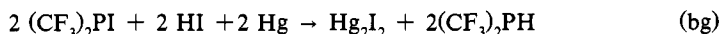
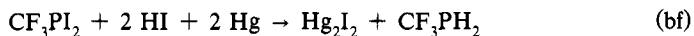
and from pentacoordinated P—H-phosphoranes⁴⁷ with F^- :



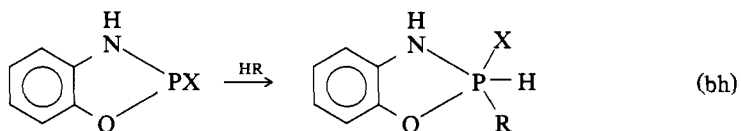
In contrast, PF_2I with PH_3 or HI ⁴⁸, or CF_3PI_2 with HI ⁴⁹ in the presence of Hg yield P(III) products:



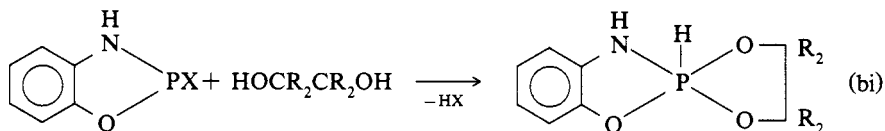
Reaction (bd) is preferable for PF_2H synthesis if PH_3 is available. Both meso and d,l-forms of $(\text{CF}_3\text{PH})_2$ are observed. With xs HI in the presence of Hg, CF_3PI_2 , or $(\text{CF}_3)_2\text{PI}$ form the respective phosphines⁴⁹:



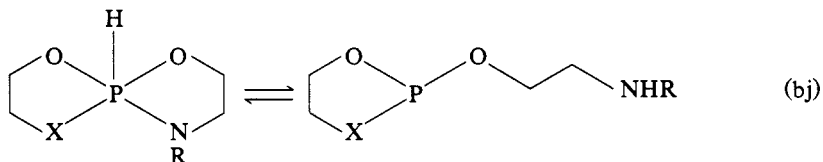
Phosphorous(V) P—H-phosphoranes, stabilized by the P atom being in at least one ring, can be synthesized; e.g., phosphonamidites react with carboxylic acids, alcohols, and thiols (HR) to form five-coordinated products^{50,51}:



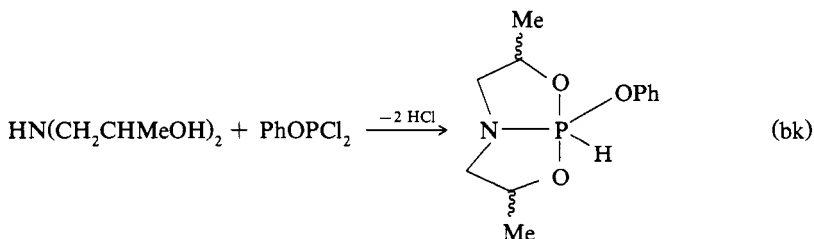
where $X = \text{Et}$; $R = \text{OEt}$, OPh , SPh , OAc , SEt , $\text{OCOCH}=\text{CH}_2$, $o\text{-NH}_2\text{C}_6\text{H}_4$. Reactions proceed in aprotic solvents (ethers, benzene, toluene, CH_2Cl_2) at reflux T. Diol reactions with phosphonamidates or Ph_2PCl proceed similarly⁵⁰:



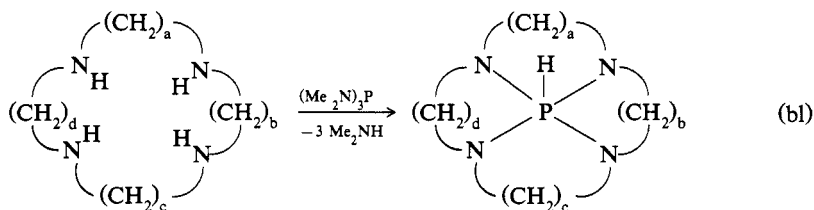
where $X = \text{NMe}_2$, $R = \text{H}$; $X = \text{N}(\text{CH}_2\text{CH}_2)_2$, $R = \text{Me}$. Equilibrium between the P—H-phosphorane and its P(III) form is observed in solution, e.g.:



Reactions between compounds with mixed hydroxyl-amino functionality and P(III) species yield P—H-phosphoranes also⁵⁰:

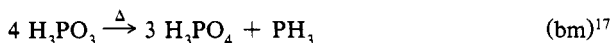


Using $\text{MeP}(\text{NMe}_2)_2$ instead of PhOPCl_2 , the product mixture consists of one d,l- and two meso-forms⁵¹. Cyclic tetramines consisting of 12 ($a-d = 2$), 13 ($a-c = 2$; $d = 3$), 14 ($a = c = 2$, $b = d = 3$), 15 ($a-c = 3$; $d = 2$) and 16 ($a-d = 3$) membered rings react with $(\text{Me}_2\text{N})_3\text{P}$ at 120°C to form tetramine P—H-phosphoranes⁵²:

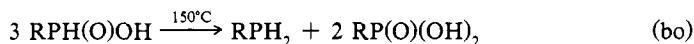


Compound stability decreases with increasing tetramine ring size.

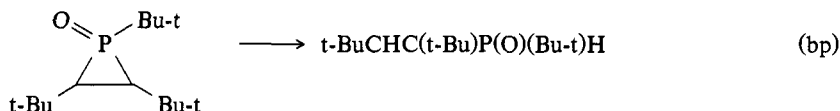
Disproportionation of proton-acidic P species can result in P—H bond formation. Anhydrous H_3PO_3 decomposes at 220°C to PH_3 and H_3PO_4 :



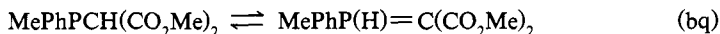
Alkyl halide reactions with NaP(OH)_2 yield alkylphosphinites⁷ which upon heating disproportionate³²:



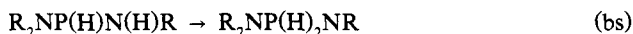
Intramolecular H-rearrangement processes yield P—H products in a phosphorane oxide rearrangement to an alkenylphosphinite⁵³:



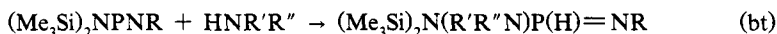
Tautomeric exchange occurs in carboxy-substituted phosphines⁵⁴ or in hydroxyphosphathenes⁵⁵, both tautomers existing in solution at equilibrium:



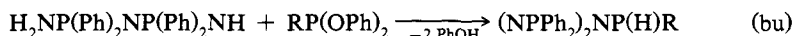
Aminophosphines containing an NHR group on phosphorus can rearrange to the P—H-phosphinimine product⁵⁶:



where R = alkyl, Me_3Si . When R = alkyl, the P(V) form dominates; however, with Me_3Si substitution or P coordination to a metal, the systems can be stabilized in the P(III) form. Dialkylamine addition to phosphinimines yields P—H products through aminophosphine intermediates⁵⁷:



where R = Me_3Si , t-Bu; R' = R'' = Me_3Si ; Et, $-(\text{CH}_2)_5-$; R', R'' = H, t-Bu. In this system, the latter predominates when R = t-Bu. Hydriodocyclophosphazenes form similarly:



where R = Me, Et, Ph.

(A.D. NORMAN)

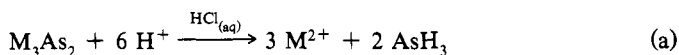
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. V. D. Bianco, S. Doronzo, *Inorg. Synth.*, **16**, 161 (1976).
3. M. Baudler, *Angew. Chem., Int. Ed. Engl.*, **21**, 492 (1982).
4. M. Baudler, C. Gruner, H. Tschähunn, J. Hahn, *Chem. Ber.*, **115**, 1739 (1982).
5. G. Huttner, H. D. Müller, V. Bejenke, O. Orama, *Z. Naturforsch., Teil B*, **31**, 1166 (1976).
6. A. E. Finholt, C. Helling, V. Imhof, L. Nielson, E. Jacobson, *Inorg. Chem.*, **2**, 504 (1963).
7. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976. Good general coverage of the chemistry of phosphorus.
8. G. Fritz, G. Becker, *Angew. Chem., Int. Ed. Engl.*, **6**, 1078 (1967).
9. I. Granoth, J. C. Martin, *J. Am. Chem. Soc.*, **101**, 4623 (1979).
10. H. R. Allcock, P. J. Harris, *J. Am. Chem. Soc.*, **101**, 6221 (1979).
11. F. Seel, H. J. Bassler, *Z. Anorg. Allg. Chem.*, **418**, 263 (1975).
12. J. W. Long, J. L. Franklin, *J. Am. Chem. Soc.*, **96**, 2370 (1974).
13. L. J. Vande Griend, J. G. Verkade, *J. Am. Chem. Soc.*, **97**, 5958 (1975).

14. D. S. Milbrath, J. G. Verkade, *J. Am. Chem. Soc.*, **99**, 6607 (1977).
15. E. W. Abel, S. M. Illingworth, *Organomet. Chem. Rev.*, **A**, **5**, 143 (1970).
16. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
17. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
18. A. D. Norman, W. L. Jolly, *Inorg. Chem.*, **18**, 1594 (1979).
19. K. G. Sharp, *J. Chem. Soc., Chem. Commun.*, 564 (1977).
20. A. D. Norman, *Inorg. Chem.*, **9**, 870 (1970).
21. G. Becker, O. Mundt, M. Rössler, E. Schneider, *Z. Anorg. Allg. Chem.*, **443**, 42 (1978).
22. R. Demuth, *Z. Anorg. Allg. Chem.*, **427**, 221 (1976).
23. H. Schaeffer, *Z. Anorg. Allg. Chem.*, **459**, 157 (1979).
24. C. Couret, J. Escudie, J. Satgé, G. Redoules, *Synth. React. Inorg. Metal-Org. Chem.*, **7**, 99 (1977).
25. G. Becker, *Z. Anorg. Allg. Chem.*, **480**, 38 (1981).
26. G. Becker, *Z. Anorg. Allg. Chem.*, **480**, 21 (1981).
27. M. Schmidt, H. J. Schroeder, *Z. Anorg. Allg. Chem.*, **378**, 185 (1970).
28. A. Trenkle, H. Vahrenkamp, *Inorg. Synth.*, **21**, 180 (1982).
29. R. G. Cavell, R. C. Dobbie, *J. Chem. Soc.*, 1308 (1967).
30. F. A. Cotton, B. A. Franz, L. Hunter, *Inorg. Chim. Acta*, **16**, 203 (1976).
31. J. Grobe, L. V. Duc, *Z. Naturforsch., Teil B*, **36**, 666 (1981).
32. A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).
33. J. A. Miller, D. Stewart, *J. Chem. Soc. Perkin Trans. 1*, 1898 (1977).
34. K. Weissmehl, H. J. Kleiner, M. Finke, U.-H. Felcht, *Angew. Chem., Int. Ed. Engl.*, **20**, 223 (1981).
35. K. C. Hansen, G. B. Sollender, C. L. Holland, *J. Org. Chem.*, **39**, 267 (1974).
36. S. D. Venkataramu, G. D. MacDonell, W. R. Purdum, M. El-Deek, K. D. Berlin, *Chem. Rev.*, **77**, 121 (1977).
37. L. Maier, *Topics in Phosphorus Chemistry*, M. Grayson, E. J. Griffith, eds., Vol. 2, Wiley-Interscience, New York, 1965, p. 43.
38. F. Seel, G. Zindler, *Z. Anorg. Allg. Chem.*, **470**, 167 (1980).
39. A. Schmidpeter, H. Rössknecht, *Chem. Ber.*, **107**, 3146 (1974).
40. R. Appel, A. Gilak, *Chem. Ber.*, **108**, 2693 (1975).
41. U. Ahrens, H. Falius, *Chem. Ber.*, **105**, 3317 (1972).
42. E. R. Falardeau, K. W. Morse, J. G. Morse, *Inorg. Chem.*, **14**, 1239 (1975).
43. D. E. J. Arnold, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1130 (1976).
44. L. F. Centofanti, R. W. Parry, *Inorg. Chem.*, **12**, 1456 (1973).
45. A. F. Janjen, J. L. Kruczynski, *Can. J. Chem.*, **57**, 1903 (1979).
46. J. F. Nixon, J. R. Swain, *Inorg. Nucl. Chem. Lett.*, **5**, 295 (1969).
47. K. O. Christie, C. J. Schrock, E. C. Curtis, *Inorg. Chem.*, **15**, 843 (1976).
48. L. Centofanti, R. W. Rudolph, *Inorg. Synth.*, **12**, 281 (1970).
49. R. C. Dobbie, P. D. Gosling, *J. Chem. Soc., Chem. Commun.*, 585 (1975).
50. S. Trippett, ed., *Organophosphorus Chemistry, Specialist Periodical Reports*, The Chemical Society, London; Vol. 9, p. 33, 1978; Vol. 10, p. 33, 1979; Vol. 11, p. 30, 1980.
51. D. Houalla, J. Mouhuch, M. Sanchez, R. Wolf, *Phosphorus*, **5**, 229 (1975).
52. T. J. Atkins, J. E. Richman, *Tetrahedron Lett.*, **52**, 5149 (1978).
53. H. Quast, M. Heuschmann, *Justus Leibigs Ann. Chem.*, 977 (1981).
54. O. I. Kolodiaznyi, *Tetrahedron Lett.*, **21**, 2269 (1980).
55. G. Becker, M. Rosler, E. Schneider, *Z. Anorg. Allg. Chem.*, **439**, 121 (1978).
56. E. Niecke, C. Ringel, *Angew. Chem., Int. Ed. Engl.*, **16**, 486 (1977).
57. A. Schmidpeter, J. Ebeling, *Angew. Chem., Int. Ed. Engl.*, **7**, 209 (1968).

1.5.3.3. of Arsenic and Arsenic Compounds

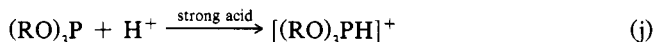
1.5.3.3.1. in Aqueous Systems.

Arsine is prepared by treatment of Mg or Zn arsenides with aqueous acid^{1,2}:

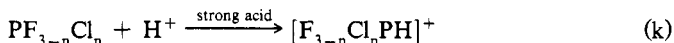


22 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.3. by Protonation
 1.5.3.2. of Phosphorus and Phosphorous Compounds

Protonation of phosphinic acid, phosphites,¹³ or halophosphines¹⁴ by FSO_3H or $\text{FSO}_3\text{H-SbF}_5$ in SO_2 at low T yields phosphonium ions, as observed in ^1H and ^{31}P NMR spectra, e.g.:



where R = H, Me, Et, i-Pr, n-Bu, Ph;



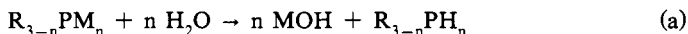
where n = 1–3.

(A.D. NORMAN)

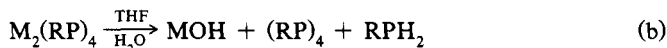
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
3. R. G. Hayter, F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).
4. R. I. Wagner, A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3869 (1953).
5. E. C. Evers, E. H. Street, Jr., S. L. Lung, *J. Am. Chem. Soc.*, **73**, 5088 (1951).
6. C. Brown, R. F. Hudson, G. A. Warten, H. Coates, *Phosphorus Sulfur*, **6**, 481 (1979).
7. D. S. Payne, in *Topics in Phosphorus Chemistry*, M. Grayson, E. J. Griffith, eds., Vol. 4, Wiley-Interscience, New York, 1967, p. 85.
8. D. C. Crofts, D. M. Parker, *J. Chem. Soc., C*, 332 (1970).
9. M. Fink, H. J. Kleiner, *Justus Leibigs Ann. Chem.*, 741 (1974).
10. T. Hata, M. Nakajima, M. Sekine, *Tetrahedron Lett.*, 2047 (1979).
11. M. E. Peach, T. C. Waddington, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 83.
12. R. J. Gillespie, E. A. Robinson, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 117.
13. G. A. Olah, C. W. McFarland, *J. Org. Chem.*, **36**, 1374 (1971).
14. L. J. Vande Griend, J. G. Verkade, *J. Am. Chem. Soc.*, **97**, 5958 (1975).

1.5.3.2.3. with Protonic Acids in Nonprotonic Solvents.

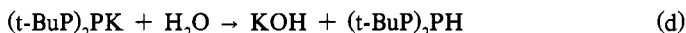
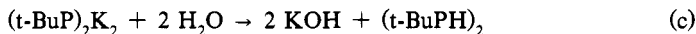
Protonation of phosphides results in direct formation of P—H bonds.^{1,2} Reactions of alkali-metal mono- and disubstituted phosphides with H_2O in ethers leads to:



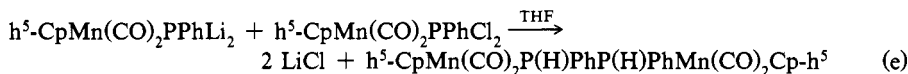
where n = 1, 2, 3; R = alkyl, aryl; M = Li, Na, K; e.g., PH_3 , PhPH_2 , Et_2PH , Ph_2PH , EtPhPH , in 30–80% yields. Metal salts of di- and tetraphosphines react to form phosphines and cyclopolyphosphines³:



where M = Li, K; R = Me, Et, C_6H_{11} . t-Butyl-substituted lithio di- and triphosphines upon hydrolysis generate the parent phosphines^{3,4}:



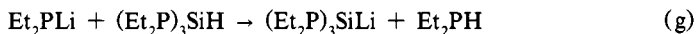
The $\text{h}^5\text{-Cp}(\text{CO})_2\text{Mn}$ -coordinated $(\text{PhPH})_2$ forms in a reaction involving an -ide salt in which protons are abstracted from the THF solvent⁵:



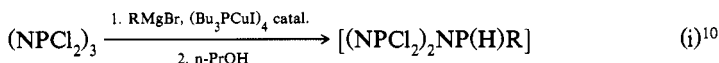
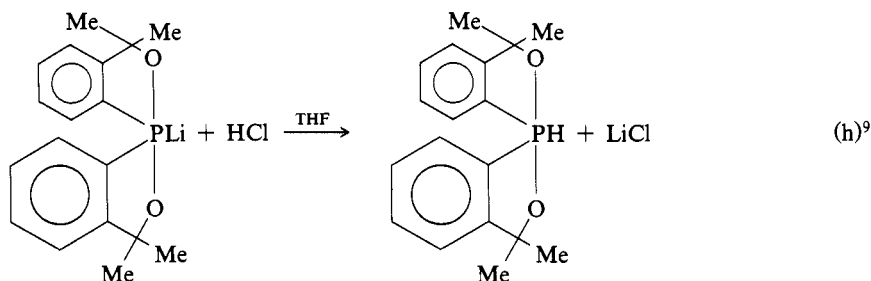
Complex phosphido- or alkylphosphidoaluminates quantitatively hydrolyze to form⁶ PH_3 or primary and secondary phosphines, e.g.:



The strongly basic Et_2PLi deprotonates $(\text{Et}_2\text{P})_3\text{SiH}$:

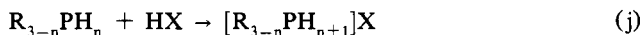


however, no reaction occurs⁸ with $(\text{Et}_2\text{P})_2\text{SiH}_2$. Reaction of HCl with a spiro-phosphorus(V) anion and treatment of the $(\text{NPCl}_2)_3$ alkylmagnesium halide reagent product with $i\text{-PrOH}$ proceed:

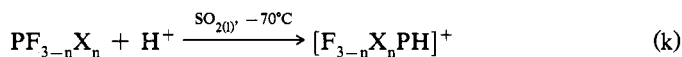


where $\text{R} = \text{Me, Et, } i\text{-Pr, } n\text{-Pr, } n\text{-Bu}$. Deuterium-labeling experiments show the P-H hydrogen comes from the $n\text{-PrOH}$.

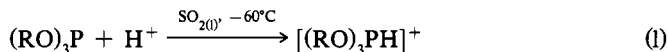
Phosphonium salts containing a P-H bond form in condensed phases upon strong-acid protonation^{1,11} or in the gas phase by hydrogen-ion protonation^{7,12} of phosphines:



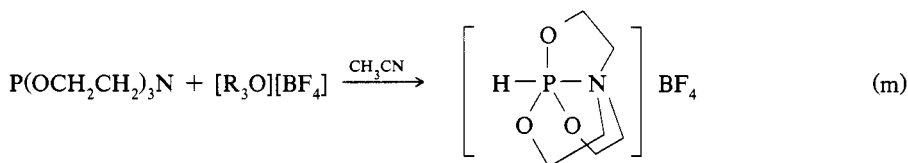
where $\text{R} = \text{H, alkyl, aryl}$; $\text{X} = \text{Cl, Br, I}$ and $n = 0-3$. The more strongly basic alkylphosphines react quantitatively. Phosphonium chloride or bromide is highly dissociated at RT; PH_4I forms a solid stable adduct¹. The perfluoroalkylphosphines are cleaved by HX to CF_3H and the respective P(III) halide. Phosphorus(III) halides and phosphites are protonated in strong acid media, e.g. $\text{HSO}_3\text{F-SbF}_5$ in SO_2 at -60°C to -70°C ¹³:



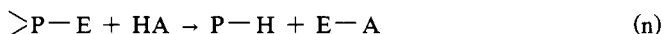
where $\text{X} = \text{Cl, } n = \text{X} = \text{Br, } n = 1-3$;



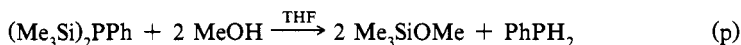
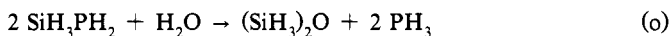
where $\text{R} = \text{Me, Et, } i\text{-Pr, } n\text{-Bu, Ph}$. Tetramethyldiphosphine is protonated¹¹ by HCl in CHCl_3 . Reaction of the P -containing cage, $\text{P}(\text{OCH}_2\text{CH}_2)_3\text{N}$, with $[\text{R}_3\text{O}][\text{BF}_4]$ in CH_3CN gives the intramolecularly P-N -coordinated cage in 80% yield¹⁴:



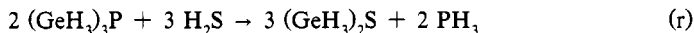
Protonic acid cleavage of bonds between P and group IVB elements (E = Si, Ge, Sn) yields P—H bonds¹⁵⁻¹⁷:



Reactions involving the acids H_2O , H_2S , ROH , RSH , NH_3 , RNH_2 , RCCH , and RCO_2H in the gas phase or in nonprotic solvents, form, e.g., $\text{R}_{3-n}\text{PH}_n$ ($n = 1-3$), PH_3 ¹⁵⁻²⁰, RPH_2 ($\text{R} = \text{Me, Et, t-Bu, Ph}$)^{15,21} and R_2PH ($\text{R} = \text{Me, Et, Ph}$)^{15,16,21,22}:



The order of acid reactivity is hydrogen halides > alcohol, thiols > amines. It is noteworthy that $(\text{GeH}_3)_3\text{P}$ is inert to H_2O cleavage but reacts rapidly¹⁶ with H_2S :



Cleavage of Si—P bonds is fast; Ge—P and Sn—P bonds are less reactive; $\text{Ph}_3\text{SnPPh}_2$ is inert¹⁵ to hot H_2O . The stepwise nature of multiple cleavage reactions can be used to prepare intermediate cleavage products, e.g., under controlled conditions both $\text{Me}_3\text{SiP(H)Ph}$:

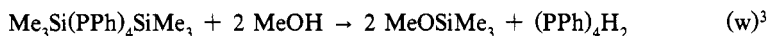
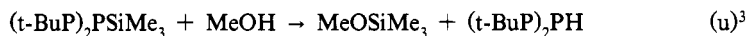


and PhPH_2 :

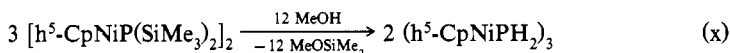


can be obtained²¹ from the alcoholysis of $(\text{Me}_3\text{Si})_2\text{PPh}$.

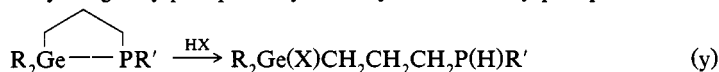
Protonic acid cleavage of group IVB element (Si, Ge)-P bonds is most valuable synthetically to prepare P—H bond-containing higher phosphines or metal complexes:



Methanolysis of silylated metal phosphido complexes yields phosphido complexes,²³ e.g.:



Acid cleavage of the cyclic germylphosphines yields acyclic secondary phosphines²⁴:

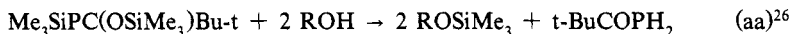


where R = Et, R' = Et, Ph; X = Cl, OH, OMe, SEt, OAc.

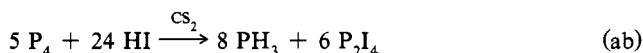
Alcohol cleavage of C—P bonds can form P—H bond-containing products. Methanol cleaves (MeCO)₃P stepwise, forming²⁵ PH₃:



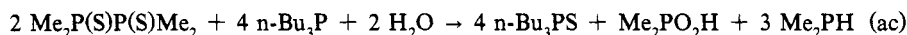
Cleavage of the P=C bond in a phosphathene proceeds:



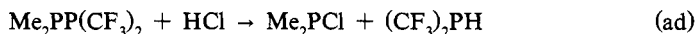
Protonic acid cleavage of the P—P bonds in P₄ yields compounds containing P—H bonds. Reaction at 25°C with HI yields PH₃ and P₂I₄ quantitatively²⁷:



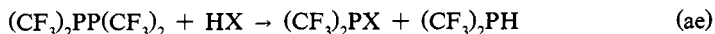
Dimethylphosphine, from H₂O cleavage of Me₂P(S)P(S)Me₂ in the presence of n-Bu₃P at 160–170°C, is obtained in 66% yield²⁸:



This synthesis of Me₂PH is better than the LiAlH₄–Me₂P(S)P(S)Me₂ method described in §1.5.5.2.2. The unsymmetrically substituted diphosphine Me₂PP(CF₃)₂ reacts with HCl:



or H₂O at 25°C, forming (CF₃)₂PH in 98% and 79% yields, respectively²⁹. Dry HI, H₂O, or Me₂AsH and (CF₃)₂PP(CF₃)₂ react:



where X = I, OH, AsMe₂. Ring opening and partial degradation of (CF₃P)₄ by H₂O in diglyme yields a mixture²⁹ of (CF₃P)₂H₂ and (CF₃P)₃H₂. Reduction–scission of Me₄P₂ by RuCl₃·x H₂O forms metal-coordinated³⁰ Me₂PH:

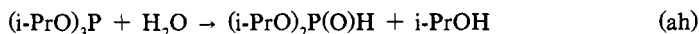


Trimethylstannane cleavage of metal-coordinated diphosphines yields metal-coordinated³¹ (CF₃)₂PH:

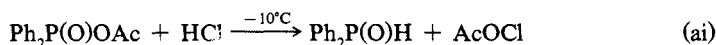


where R = Me, CF₃; M = Cr, Mo.

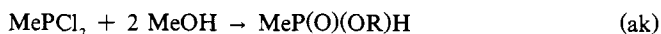
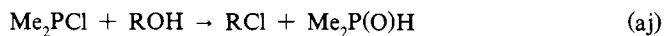
Hydrolysis or alcoholysis of P(III) halides, especially PCl₃ and PBr₃, yields H₃PO₃; however, these reactions are better carried out in H₂O or alcoholic media^{1,7} (see §1.5.3.2.1 and §1.5.3.2.2). Hydrolysis of trialkyl or triarylphosphites occurs readily, e.g., reaction⁷ of (i-PrO)₃P with H₂O in CH₃CN:



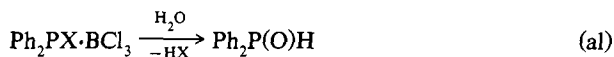
Dry HCl reacts with Ph₂P(O)Ac, yielding Ph₂P(O)H³³:



Controlled reactions of Me₂PCL with H₂O or MeOH and MePCL₂ with MeOH³⁴ yield Me₂P(O)H and MeP(O)HOMe, respectively:

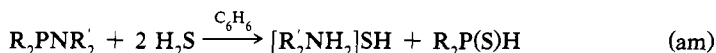


where R = H, Me. Boron-trichloride coordination of tertiary Ph_2PX phosphines, followed by addition of H_2O , produces $\text{Ph}_2\text{P(O)H}$ in 68–87% yield³⁵:

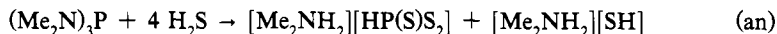


where X = CH_2OMe , CH_2SMe , C(O)Ph . Hydrolysis of cyclic secondary phosphine chlorides results in the cyclic phosphine oxide in high yield³⁶.

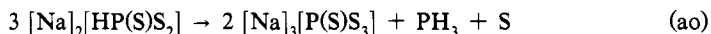
Aminophosphines can react with protonic acids (HX) to form P—H bonds. Generally, such reactions produce NH and PX products, owing to the polarity of the P—N bond^{1,37}. Hydrogen sulfide and dialkylaminodialkylphosphines in benzene at 80°C yield dialkylphosphine sulfides quantitatively³⁷:



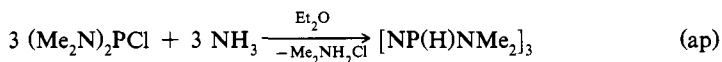
where R = Et; R' = Me, Et, t-Bu, Ph. Tris(dimethylamino)phosphine reacts with H_2S :



Conversion of thiophosphite to its Na salt, followed by thermolysis, yields PH_3 quantitatively³⁸:

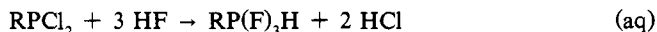


Ammonia and $(\text{Me}_2\text{N})_2\text{PCl}$ in diethyl ether form the hydridocyclophosphazene³⁹:



An aminophosphine intermediate forms, which tautomerizes to the final product.

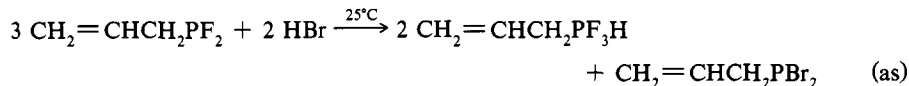
Oxidative addition of protonic acids to P(III) compounds yields P—H-phosphoranes. Alkyldichlorophosphines react at –30 to –20°C with HF in CCl_3 solvent to form equatorially substituted products⁴⁰:



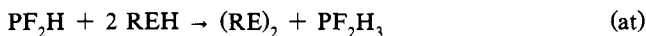
where R = Me, Et, n-Bu, t-Bu, Ph. In the presence of H_2O , the phosphonous acid fluorides forms⁴¹:



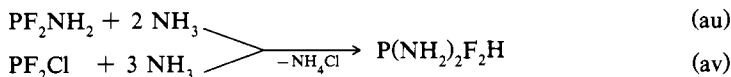
Gaseous HBr and allyldifluorophosphine undergo exchange and addition⁴²:



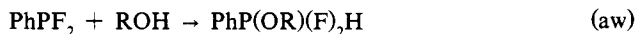
Gaseous NH_3 and PF_2NH_2 or PF_2Cl react⁴³ at 25°C. Alcohols and thiols, with PF_2H at 0°C, form⁴⁴ PH_2F_2 :



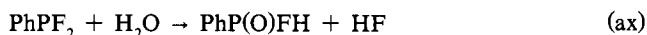
where R = Me, Et; E = O, S;



Alcohols react with PhPF_2 in benzene to form P—H-fluorophosphoranes⁴⁵:



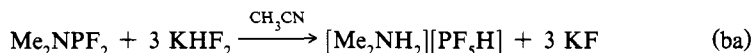
where R = Me, Et, CF_3CH_2 , $(\text{CF}_3)_2\text{CH}$, $\text{Ph}(\text{CF}_3)\text{CH}$, t-Bu, whereas H_2O reacts in a two-step process to produce the final PhPF_3H :



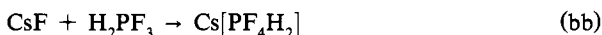
Six-coordinated P—H-phosphoranes form⁴⁶ P(III) compounds and from $[\text{HF}_2]^-$:



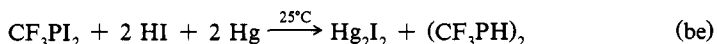
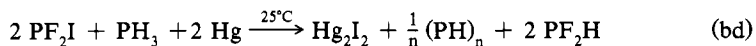
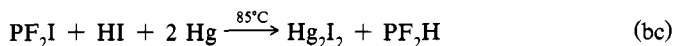
where n = 0,1,2; or from:



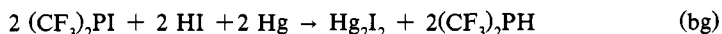
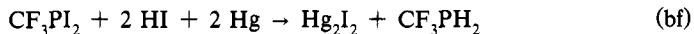
and from pentacoordinated P—H-phosphoranes⁴⁷ with F^- :



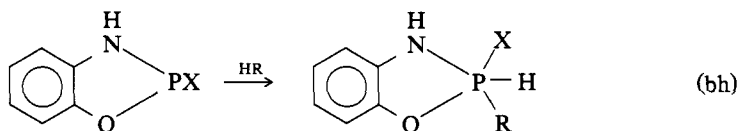
In contrast, PF_2I with PH_3 or HI ⁴⁸, or CF_3PI_2 with HI ⁴⁹ in the presence of Hg yield P(III) products:



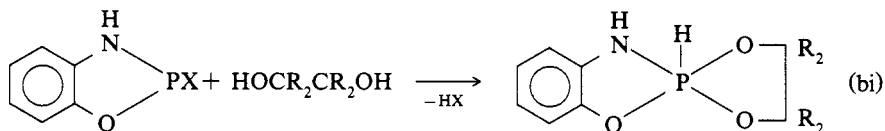
Reaction (bd) is preferable for PF_2H synthesis if PH_3 is available. Both meso and d,l-forms of $(\text{CF}_3\text{PH})_2$ are observed. With xs HI in the presence of Hg, CF_3PI_2 , or $(\text{CF}_3)_2\text{PI}$ form the respective phosphines⁴⁹:



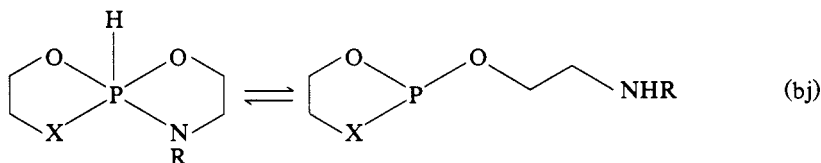
Phosphorous(V) P—H-phosphoranes, stabilized by the P atom being in at least one ring, can be synthesized; e.g., phosphonamidites react with carboxylic acids, alcohols, and thiols (HR) to form five-coordinated products^{50,51}:



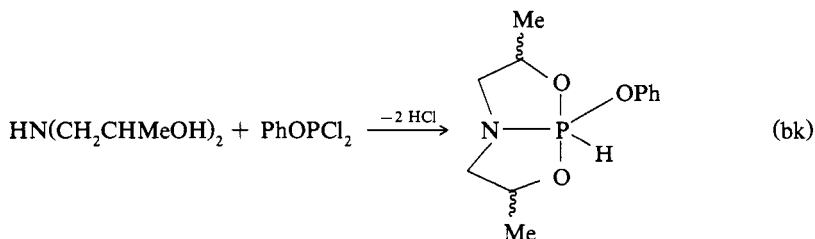
where $X = \text{Et}$; $R = \text{OEt}$, OPh , SPh , OAc , SEt , $\text{OCOCH}=\text{CH}_2$, $\text{o-NH}_2\text{C}_6\text{H}_4$. Reactions proceed in aprotic solvents (ethers, benzene, toluene, CH_2Cl_2) at reflux T. Diol reactions with phosphonamidates or Ph_2PCl proceed similarly⁵⁰:



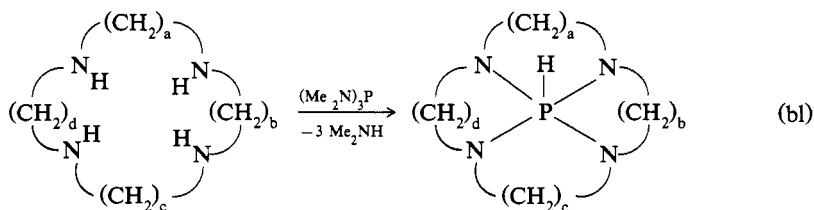
where $X = \text{NMe}_2$, $R = \text{H}$; $X = \text{N}(\text{CH}_2\text{CH}_2)_2$, $R = \text{Me}$. Equilibrium between the P—H-phosphorane and its P(III) form is observed in solution, e.g.:



Reactions between compounds with mixed hydroxyl-amino functionality and P(III) species yield P—H-phosphoranes also⁵⁰:

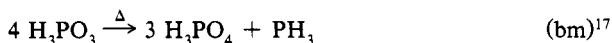


Using $\text{MeP}(\text{NMe}_2)_2$ instead of PhOPCl_2 , the product mixture consists of one d,l- and two meso-forms⁵¹. Cyclic tetramines consisting of 12 ($a-d = 2$), 13 ($a-c = 2$; $d = 3$), 14 ($a = c = 2$, $b = d = 3$), 15 ($a-c = 3$; $d = 2$) and 16 ($a-d = 3$) membered rings react with $(\text{Me}_2\text{N})_3\text{P}$ at 120°C to form tetramine P—H-phosphoranes⁵²:

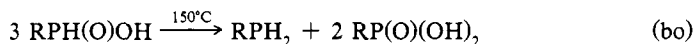


Compound stability decreases with increasing tetramine ring size.

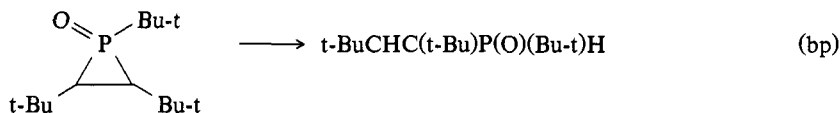
Disproportionation of proton-acidic P species can result in P—H bond formation. Anhydrous H_3PO_3 decomposes at 220°C to PH_3 and H_3PO_4 :



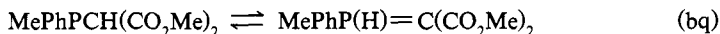
Alkyl halide reactions with NaP(OH)_2 yield alkylphosphinites⁷ which upon heating disproportionate³²:



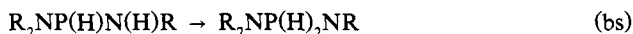
Intramolecular H-rearrangement processes yield P—H products in a phosphorane oxide rearrangement to an alkenylphosphinite⁵³:



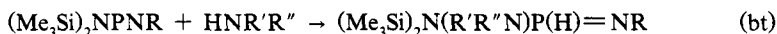
Tautomeric exchange occurs in carboxy-substituted phosphines⁵⁴ or in hydroxyphosphathenes⁵⁵, both tautomers existing in solution at equilibrium:



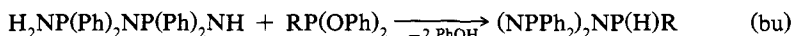
Aminophosphines containing an NHR group on phosphorus can rearrange to the P—H-phosphinimine product⁵⁶:



where R = alkyl, Me_3Si . When R = alkyl, the P(V) form dominates; however, with Me_3Si substitution or P coordination to a metal, the systems can be stabilized in the P(III) form. Dialkylamine addition to phosphinimines yields P—H products through aminophosphine intermediates⁵⁷:



where R = Me_3Si , t-Bu; R' = R'' = Me_3Si ; Et, $-(\text{CH}_2)_5-$; R', R'' = H, t-Bu. In this system, the latter predominates when R = t-Bu. Hydriodocyclophosphazenes form similarly:



where R = Me, Et, Ph.

(A.D. NORMAN)

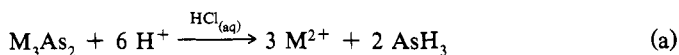
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. V. D. Bianco, S. Doronzo, *Inorg. Synth.*, **16**, 161 (1976).
3. M. Baudler, *Angew. Chem., Int. Ed. Engl.*, **21**, 492 (1982).
4. M. Baudler, C. Gruner, H. Tschähunn, J. Hahn, *Chem. Ber.*, **115**, 1739 (1982).
5. G. Huttner, H. D. Müller, V. Bejenke, O. Orama, *Z. Naturforsch., Teil B*, **31**, 1166 (1976).
6. A. E. Finholt, C. Helling, V. Imhof, L. Nielson, E. Jacobson, *Inorg. Chem.*, **2**, 504 (1963).
7. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976. Good general coverage of the chemistry of phosphorus.
8. G. Fritz, G. Becker, *Angew. Chem., Int. Ed. Engl.*, **6**, 1078 (1967).
9. I. Granoth, J. C. Martin, *J. Am. Chem. Soc.*, **101**, 4623 (1979).
10. H. R. Allcock, P. J. Harris, *J. Am. Chem. Soc.*, **101**, 6221 (1979).
11. F. Seel, H. J. Bassler, *Z. Anorg. Allg. Chem.*, **418**, 263 (1975).
12. J. W. Long, J. L. Franklin, *J. Am. Chem. Soc.*, **96**, 2370 (1974).
13. L. J. Vande Griend, J. G. Verkade, *J. Am. Chem. Soc.*, **97**, 5958 (1975).

14. D. S. Milbrath, J. G. Verkade, *J. Am. Chem. Soc.*, **99**, 6607 (1977).
15. E. W. Abel, S. M. Illingworth, *Organomet. Chem. Rev.*, **A**, **5**, 143 (1970).
16. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
17. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
18. A. D. Norman, W. L. Jolly, *Inorg. Chem.*, **18**, 1594 (1979).
19. K. G. Sharp, *J. Chem. Soc., Chem. Commun.*, 564 (1977).
20. A. D. Norman, *Inorg. Chem.*, **9**, 870 (1970).
21. G. Becker, O. Mundt, M. Rössler, E. Schneider, *Z. Anorg. Allg. Chem.*, **443**, 42 (1978).
22. R. Demuth, *Z. Anorg. Allg. Chem.*, **427**, 221 (1976).
23. H. Schaeffer, *Z. Anorg. Allg. Chem.*, **459**, 157 (1979).
24. C. Couret, J. Escudie, J. Satgé, G. Redoules, *Synth. React. Inorg. Metal-Org. Chem.*, **7**, 99 (1977).
25. G. Becker, *Z. Anorg. Allg. Chem.*, **480**, 38 (1981).
26. G. Becker, *Z. Anorg. Allg. Chem.*, **480**, 21 (1981).
27. M. Schmidt, H. J. Schroeder, *Z. Anorg. Allg. Chem.*, **378**, 185 (1970).
28. A. Trenkle, H. Vahrenkamp, *Inorg. Synth.*, **21**, 180 (1982).
29. R. G. Cavell, R. C. Dobbie, *J. Chem. Soc.*, 1308 (1967).
30. F. A. Cotton, B. A. Franz, L. Hunter, *Inorg. Chim. Acta*, **16**, 203 (1976).
31. J. Grobe, L. V. Duc, *Z. Naturforsch., Teil B*, **36**, 666 (1981).
32. A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).
33. J. A. Miller, D. Stewart, *J. Chem. Soc. Perkin Trans. 1*, 1898 (1977).
34. K. Weissmehl, H. J. Kleiner, M. Finke, U.-H. Felcht, *Angew. Chem., Int. Ed. Engl.*, **20**, 223 (1981).
35. K. C. Hansen, G. B. Sollender, C. L. Holland, *J. Org. Chem.*, **39**, 267 (1974).
36. S. D. Venkataramu, G. D. MacDonell, W. R. Purdum, M. El-Deek, K. D. Berlin, *Chem. Rev.*, **77**, 121 (1977).
37. L. Maier, *Topics in Phosphorus Chemistry*, M. Grayson, E. J. Griffith, eds., Vol. 2, Wiley-Interscience, New York, 1965, p. 43.
38. F. Seel, G. Zindler, *Z. Anorg. Allg. Chem.*, **470**, 167 (1980).
39. A. Schmidpeter, H. Rössknecht, *Chem. Ber.*, **107**, 3146 (1974).
40. R. Appel, A. Gilak, *Chem. Ber.*, **108**, 2693 (1975).
41. U. Ahrens, H. Falius, *Chem. Ber.*, **105**, 3317 (1972).
42. E. R. Falardeau, K. W. Morse, J. G. Morse, *Inorg. Chem.*, **14**, 1239 (1975).
43. D. E. J. Arnold, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1130 (1976).
44. L. F. Centofanti, R. W. Parry, *Inorg. Chem.*, **12**, 1456 (1973).
45. A. F. Janjen, J. L. Kruczynski, *Can. J. Chem.*, **57**, 1903 (1979).
46. J. F. Nixon, J. R. Swain, *Inorg. Nucl. Chem. Lett.*, **5**, 295 (1969).
47. K. O. Christie, C. J. Schrock, E. C. Curtis, *Inorg. Chem.*, **15**, 843 (1976).
48. L. Centofanti, R. W. Rudolph, *Inorg. Synth.*, **12**, 281 (1970).
49. R. C. Dobbie, P. D. Gosling, *J. Chem. Soc., Chem. Commun.*, 585 (1975).
50. S. Trippett, ed., *Organophosphorus Chemistry, Specialist Periodical Reports*, The Chemical Society, London; Vol. 9, p. 33, 1978; Vol. 10, p. 33, 1979; Vol. 11, p. 30, 1980.
51. D. Houalla, J. Mouhuch, M. Sanchez, R. Wolf, *Phosphorus*, **5**, 229 (1975).
52. T. J. Atkins, J. E. Richman, *Tetrahedron Lett.*, **52**, 5149 (1978).
53. H. Quast, M. Heuschmann, *Justus Leibigs Ann. Chem.*, 977 (1981).
54. O. I. Kolodiaznyi, *Tetrahedron Lett.*, **21**, 2269 (1980).
55. G. Becker, M. Rosler, E. Schneider, *Z. Anorg. Allg. Chem.*, **439**, 121 (1978).
56. E. Niecke, C. Ringel, *Angew. Chem., Int. Ed. Engl.*, **16**, 486 (1977).
57. A. Schmidpeter, J. Ebeling, *Angew. Chem., Int. Ed. Engl.*, **7**, 209 (1968).

1.5.3.3. of Arsenic and Arsenic Compounds

1.5.3.3.1. in Aqueous Systems.

Arsine is prepared by treatment of Mg or Zn arsenides with aqueous acid^{1,2}:



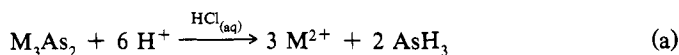
30 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
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14. D. S. Milbrath, J. G. Verkade, *J. Am. Chem. Soc.*, **99**, 6607 (1977).
15. E. W. Abel, S. M. Illingworth, *Organomet. Chem. Rev.*, **A**, **5**, 143 (1970).
16. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
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18. A. D. Norman, W. L. Jolly, *Inorg. Chem.*, **18**, 1594 (1979).
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22. R. Demuth, *Z. Anorg. Allg. Chem.*, **427**, 221 (1976).
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31. J. Grobe, L. V. Duc, *Z. Naturforsch., Teil B*, **36**, 666 (1981).
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Arsine is prepared by treatment of Mg or Zn arsenides with aqueous acid^{1,2}:



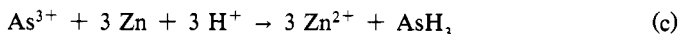
Using an Mg-Al-As alloy low yields of As_2H_4 in addition to AsH_3 arise². Slow addition of H_2O to powdered Na_3As at 25°C produces AsH_3 in 85–90% yield³:



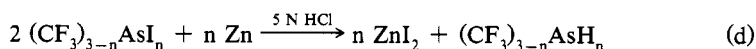
along with traces of As_2H_4 . Hydrolysis of mixed $\text{CaGe-Ca}_3\text{As}_2$ alloys produces small amounts of GeH_3AsH_2 , along with binary hydrides².

Reactions of As metal, As_4O_6 , or As(III) halides with H_2O do not yield As—H bonds, in contrast to the P analogues (see §1.5.3.2.1).

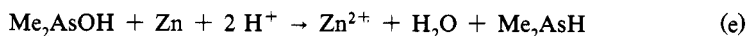
Arsine forms upon reduction of As(III) species in acid⁴:



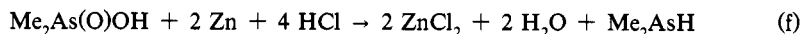
Phenylarsonic acid reacts with Zn amalgam in H_2O to form PhAsH_2 in 83% yield¹. Similarly, Cu-Zn alloy in acid reduces CF_3AsI_2 and $(\text{CF}_3)_2\text{AsI}$ to CF_3AsH_2 and $(\text{CF}_3)_2\text{AsH}$, respectively⁵:



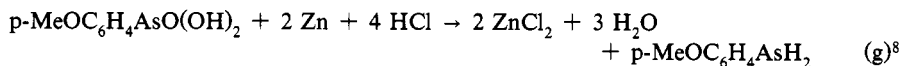
where $n = 1, 2$. Zinc dust in acid reduces Me_2AsOH :



or $\text{Me}_2\text{As(O)OH}$ (cacodylic acid) to Me_2AsH nearly quantitatively^{6,7}:



Zinc amalgam reduction of $\text{PhMeAsO}_2\text{H}$ yields PhMeAsH . Reduction of the arsonic acid function, without attack on the substituted aryl ring, yields $p\text{-MeC}_6\text{H}_4\text{AsH}_2$:



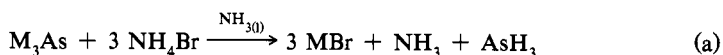
Electrolytic reduction of As(III) or As(V) species in solution at the cathode yields arsine^{2,9}; e.g., AsH_3 is formed upon reduction of either As(III) or As(V) species in 0.5 N H_2SO_4 . Reduction of As(V) is more cathodic than As(III).

(A.D. NORMAN)

1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
3. J. E. Drake, C. Riddle, *Inorg. Synth.*, **13**, 14 (1972). A preferred synthesis of AsH_3 .
4. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York, 1970.
5. H. J. Emeléus, R. N. Hazeldine, E. Walaschewski, *J. Chem. Soc.*, 1552 (1953).
6. R. D. Feltham, A. Kasenally, R. S. Nyholm, *J. Organomet. Chem.*, **7**, 285 (1967).
7. R. D. Feltham, W. Silverthorne, *Inorg. Synth.*, **10**, 159 (1967).
8. F. G. Mann, A. J. Wilkinson, *J. Chem. Soc.*, 3336 (1957).
9. V. P. Gladyshev, *Tr. Inst. Khim. Nauk Akad. Nauk, Kaz., SSR.*, **35**, 74 (1973); *Chem. Abstr.*, **80**, 43,447 (1974).

1.5.3.3.2. in Other Protonic Solvents.

Alkali-metal arsenides M_3As in liq NH_3 react with NH_4Br to form^{1,2} AsH_3 :



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 31
 1.5.3. by Protonation
 1.5.3.3. of Arsenic and Arsenic Compounds

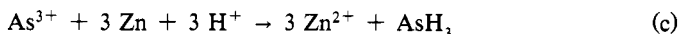
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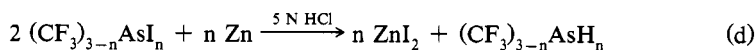
along with traces of As_2H_4 . Hydrolysis of mixed CaGe-Ca₃As₂ alloys produces small amounts of GeH_3AsH_2 , along with binary hydrides².

Reactions of As metal, As_4O_6 , or As(III) halides with H_2O do not yield As—H bonds, in contrast to the P analogues (see §1.5.3.2.1).

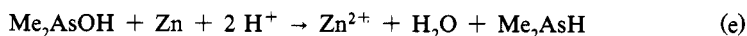
Arsine forms upon reduction of As(III) species in acid⁴:



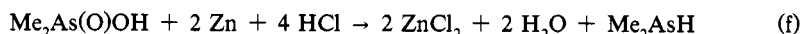
Phenylarsonic acid reacts with Zn amalgam in H_2O to form PhAsH_2 in 83% yield¹. Similarly, Cu-Zn alloy in acid reduces CF_3AsI_2 and $(\text{CF}_3)_2\text{AsI}$ to CF_3AsH_2 and $(\text{CF}_3)_2\text{AsH}$, respectively⁵:



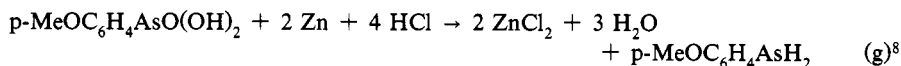
where $n = 1, 2$. Zinc dust in acid reduces Me_2AsOH :



or $\text{Me}_2\text{As(O)OH}$ (cacodylic acid) to Me_2AsH nearly quantitatively^{6,7}:



Zinc amalgam reduction of $\text{PhMeAsO}_2\text{H}$ yields PhMeAsH . Reduction of the arsonic acid function, without attack on the substituted aryl ring, yields $p\text{-MeC}_6\text{H}_4\text{AsH}_2$:



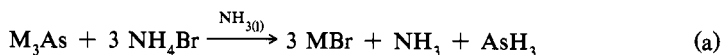
Electrolytic reduction of As(III) or As(V) species in solution at the cathode yields arsine^{2,9}; e.g., AsH_3 is formed upon reduction of either As(III) or As(V) species in 0.5 N H_2SO_4 . Reduction of As(V) is more cathodic than As(III).

(A.D. NORMAN)

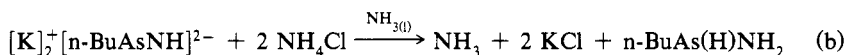
1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
3. J. E. Drake, C. Riddle, *Inorg. Synth.*, **13**, 14 (1972). A preferred synthesis of AsH_3 .
4. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York, 1970.
5. H. J. Emeléus, R. N. Hazeldine, E. Walaschewski, *J. Chem. Soc.*, 1552 (1953).
6. R. D. Feltham, A. Kasenally, R. S. Nyholm, *J. Organomet. Chem.*, **7**, 285 (1967).
7. R. D. Feltham, W. Silverthorne, *Inorg. Synth.*, **10**, 159 (1967).
8. F. G. Mann, A. J. Wilkinson, *J. Chem. Soc.*, 3336 (1957).
9. V. P. Gladyshev, *Tr. Inst. Khim. Nauk Akad. Nauk, Kaz., SSR.*, **35**, 74 (1973); *Chem. Abstr.*, **80**, 43,447 (1974).

1.5.3.3.2. in Other Protonic Solvents.

Alkali-metal arsenides M_3As in liq NH_3 react with NH_4Br to form^{1,2} AsH_3 :

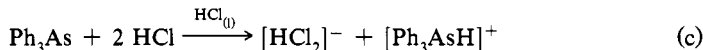


where M = Na, K. The dipotassium salt, $[K]_2^+[n\text{-BuAsNH}]^{2-}$ is protonated by NH_4Cl in NH_3 :



The aminoarsine product, readily decomposes to NH_3 and a cyclopolyarsine³.

Strong-acid protonation of t-alkyl- or arylarsines yields arsonium ions in solution⁴:



(A.D. NORMAN)

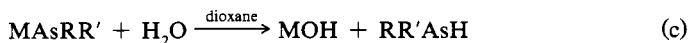
1. G. Brauer, ed., *Handbook of Preparative Inorganic Chemistry*, 2nd ed., Vol. 1, Academic Press, New York, 1963.
2. W. C. Johnson, A. Petchukas, *J. Am. Chem. Soc.*, **59**, 2068 (1937).
3. B. Ross, W. Marzi, W. Axmacher, *Chem. Ber.*, **113**, 292B (1980).
4. M. E. Peach, T. C. Waddington, in *Non-Aqueous Solvent Systems*, T. C. Waddington, ed., Academic Press, London, 1965, p. 83.

1.5.3.3.3. with Protonic Acids in Nonprotonic Solvents.

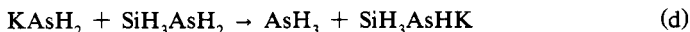
Protonation of metal arsenides provides high yields of AsH_3 and alkyl- or arylarsines^{1,4}. These reactions, by substitution of D_2O for H_2O , are especially useful sources of deuterium-labeled products:



Hydrolysis of $\text{RR}'\text{AsM}$ in dioxane at 25°C yields, e.g., the arsines² Me_2AsH , Et_2AsH , Ph_2AsH , $(\text{C}_6\text{H}_{11})_2\text{AsH}$, EtPhAsH and $(p\text{-MeC}_6\text{H}_4)_2\text{AsH}$:



where M = Li, Na, K; R and R' = alkyl or aryl. Protonation of KAsH_2 by SiH_3AsH_2 yields AsH_3 , in a proton exchange⁶:



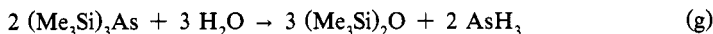
Protonic acid (HX) cleavage of arsenic-group IVB (Si, Ge, Sn) bonds in silyl-, germyl- or stannylarsines yields⁴ AsH_3 or Me_2AsH :



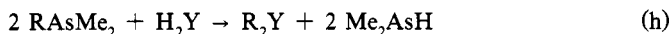
where R = SiH_3 , GeH_3 , Me_3Si ;



where R = GeH_3 , SiF_3 , Me_3Si , Me_3Ge , MeSiH_2 , MeGeH_2 ; R' = H, alkyl. Water, H_2S , ROH or RSH also react to form arsines^{3,4,6}, e.g., $(\text{Me}_3\text{Si})_3\text{As}$ and H_2O :



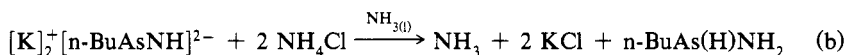
yield AsH_3 , $\text{Me}_3\text{SiAsMe}_2$ and H_2O , or $\text{Me}_2\text{AsSiF}_3$ and H_2S yield Me_2AsH :



where R = Me_3Si , Y = O; R = SiF_3 , Y = S. These cleavages are general except that Ge—P and Sn—P bonds are resistant to H_2O .

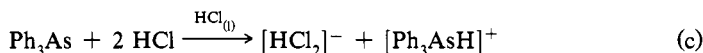
32 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.3. by Protonation
 1.5.3.3. of Arsenic and Arsenic Compounds

where M = Na, K. The dipotassium salt, $[K]_2^+[n\text{-BuAsNH}]^{2-}$ is protonated by NH_4Cl in NH_3 :



The aminoarsine product, readily decomposes to NH_3 and a cyclopolyarsine³.

Strong-acid protonation of t-alkyl- or arylarsines yields arsonium ions in solution⁴:



(A.D. NORMAN)

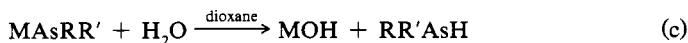
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1.5.3.3.3. with Protonic Acids in Nonprotonic Solvents.

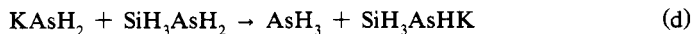
Protonation of metal arsenides provides high yields of AsH_3 and alkyl- or arylarsines^{1,4}. These reactions, by substitution of D_2O for H_2O , are especially useful sources of deuterium-labeled products:



Hydrolysis of $\text{RR}'\text{AsM}$ in dioxane at 25°C yields, e.g., the arsines² Me_2AsH , Et_2AsH , Ph_2AsH , $(\text{C}_6\text{H}_{11})_2\text{AsH}$, EtPhAsH and $(p\text{-MeC}_6\text{H}_4)_2\text{AsH}$:



where M = Li, Na, K; R and R' = alkyl or aryl. Protonation of KAsH_2 by SiH_3AsH_2 yields AsH_3 , in a proton exchange⁶:



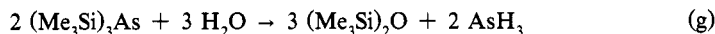
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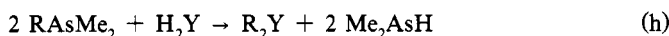
where R = SiH_3 , GeH_3 , Me_3Si ;



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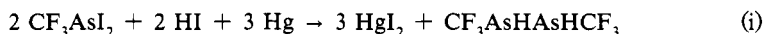


yield AsH_3 , $\text{Me}_3\text{SiAsMe}_2$ and H_2O , or $\text{Me}_2\text{AsSiF}_3$ and H_2S yield Me_2AsH :

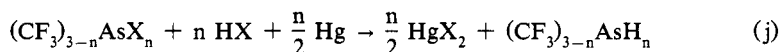


where R = Me_3Si , Y = O; R = SiF_3 , Y = S. These cleavages are general except that Ge—P and Sn—P bonds are resistant to H_2O .

Hydrogen iodide reacts with CF_3AsI_2 or $(\text{CF}_3)_2\text{AsI}$ in the presence of Hg to form arsines. A deficiency of HI with CF_3AsI_2 yields the diarsine which is present both in meso- and d,l-forms⁷:

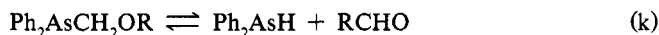


With xs HI or HCl, CF_3AsX_2 and $(\text{CF}_3)_2\text{AsX}$ yield the respective arsines^{4,8}:



where $\text{X} = \text{Cl}, \text{I}$; $n = 1, 2$.

Intramolecular proton transfer and C—As bond cleavage in the alkoxymethylarsines, $\text{Ph}_2\text{AsCH}_2\text{OR}$, results in the equilibrium formation of Ph_2AsH :



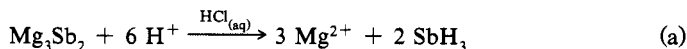
where $\text{R} = \text{Et}, \text{Ph}$. At 25°C in benzene, the equilibrium constant for the reaction is⁹ $K \approx 1$.

(A.D. NORMAN)

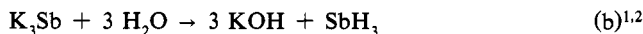
1. A. Tzschach, W. Voightlander, *Z. Chem.*, **19**, 393 (1979). A current review of the use of arsines for arsine synthesis.
2. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York, 1971.
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8. R. G. Cavell, R. C. Dobbie, *J. Chem. Soc., A*, 1308 (1967).
9. P. J. Busse, C.-P. Hsung, K. J. Irgolic, D. H. O'Brien, F. L. Kolar, *J. Organomet. Chem.*, **185**, 1 (1980).

1.5.3.4. of Antimony and Antimony Compounds.

Stibine forms from reaction of dil HCl with finely divided Mg-Sb alloy¹⁻³:



Yields are not over 10%.³ Protonic acids react with alkali-metal stibnides, e.g.:



where $\text{R} = \text{Me}, \text{Et}, \text{Ph}$, etc.

Cleavage of the Si—Sb or Ge—Sb bonds of $(\text{MH}_3)_3\text{Sb}$ ($\text{M} = \text{Si}, \text{Ge}$) with HCl results in SbH_3 in high yield⁴:



The electrolytic reduction of Sb(III) or Sb(V) species in alkali or acid yields SbH_3 at the cathode^{1,5}:

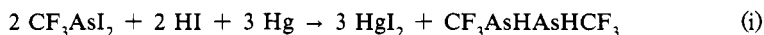


Using a metallic Sb cathode, yields up to 15% of the total gas ($\text{SbH}_3 + \text{H}_2$) can be

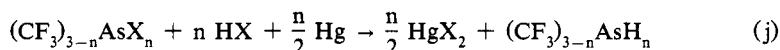
1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 33

1.5.3. by Protonation

Hydrogen iodide reacts with CF_3AsI_2 or $(\text{CF}_3)_2\text{AsI}$ in the presence of Hg to form arsines. A deficiency of HI with CF_3AsI_2 yields the diarsine which is present both in meso- and d,l-forms⁷:

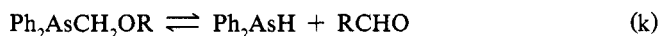


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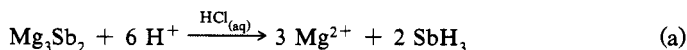
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(A.D. NORMAN)

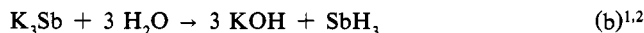
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1.5.3.4. of Antimony and Antimony Compounds.

Stibine forms from reaction of dil HCl with finely divided Mg-Sb alloy¹⁻³:



Yields are not over 10%.³ Protonic acids react with alkali-metal stibnides, e.g.:



where R = Me, Et, Ph, etc.

Cleavage of the Si—Sb or Ge—Sb bonds of $(\text{MH}_3)_3\text{Sb}$ (M = Si, Ge) with HCl results in SbH_3 in high yield⁴:

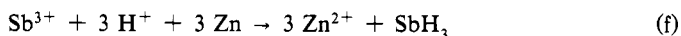


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Using a metallic Sb cathode, yields up to 15% of the total gas ($\text{SbH}_3 + \text{H}_2$) can be

attained⁵. Active metal (e.g., Na or Zn amalgam) reduction of Sb(III) in H₂O produces SbH₃:

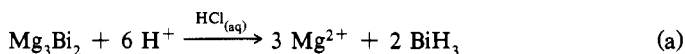


(A.D. NORMAN)

1. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, 4, 1 (1968).
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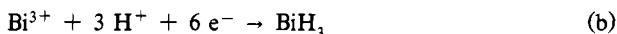
1.5.3.5. of Bismuth and Bismuth Compounds.

Bismuthine forms in low yields when dil HCl is added to a Mg-Bi alloy of approximate composition^{1,2} Mg₃Bi₂:

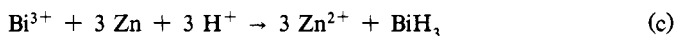


Water reacts with (Me₃Ge)₃Bi at 25°C without formation³ of BiH₃³, because of the high thermal instability of the latter.

Electrolytic reduction of Bi(III) in H₂O yields BiH₃ at the cathode¹:



Similarly, Na or Zn amalgams in 1 N H₂SO₄ or HClO₄ containing complexing agents such as thiourea yield BiH₃ at the electrode surface⁴:



(A.D. NORMAN)

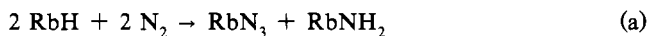
1. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, 4, 1 (1968).
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3. I. Schuman-Rudisch, *Z. Naturforsch., Teil B*, 22, 1081 (1967).
4. A. Barikov, V. P. Gladyshev, *Sov. Electrochem. (Engl. Transl.)*, 8, 795 (1972); *Chem. Abstr.*, 77, 42,368 (1972).

1.5.4. by Reaction of Hydrides

1.5.4.1. with Compounds of Nitrogen

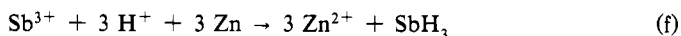
1.5.4.1.1. Involving Ionic Hydrides.

Cesium and Rb hydrides react with anhyd N₂ on heating to form metal-amide salts^{1,2}:



The other alkali-metal hydrides do not react similarly; e.g., LiH with N₂ yields Li₃N

attained⁵. Active metal (e.g., Na or Zn amalgam) reduction of Sb(III) in H₂O produces SbH₃:

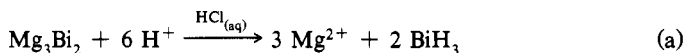


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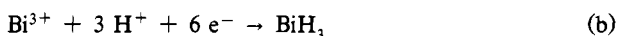
1.5.3.5. of Bismuth and Bismuth Compounds.

Bismuthine forms in low yields when dil HCl is added to a Mg-Bi alloy of approximate composition^{1,2} Mg₃Bi₂:

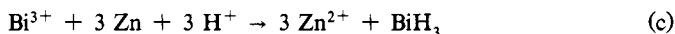


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1.5.4. by Reaction of Hydrides

1.5.4.1. with Compounds of Nitrogen

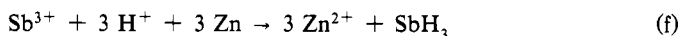
1.5.4.1.1. Involving Ionic Hydrides.

Cesium and Rb hydrides react with anhyd N₂ on heating to form metal-amide salts^{1,2}:



The other alkali-metal hydrides do not react similarly; e.g., LiH with N₂ yields Li₃N

attained⁵. Active metal (e.g., Na or Zn amalgam) reduction of Sb(III) in H₂O produces SbH₃:

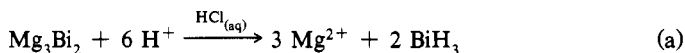


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2. G. Brauer, ed., *Handbook of Preparative Inorganic Chemistry*, 2nd ed., Vol. 1, Academic Press, New York, 1963.
3. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
4. E. A. V. Ebsworth, D. W. H. Rankin, G. M. Sheldrick, *J. Chem. Soc., A*, 2828 (1968).
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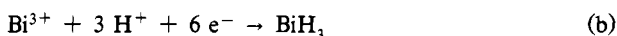
1.5.3.5. of Bismuth and Bismuth Compounds.

Bismuthine forms in low yields when dil HCl is added to a Mg-Bi alloy of approximate composition^{1,2} Mg₃Bi₂:

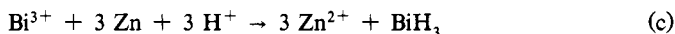


Water reacts with (Me₃Ge)₃Bi at 25°C without formation³ of BiH₃³, because of the high thermal instability of the latter.

Electrolytic reduction of Bi(III) in H₂O yields BiH₃ at the cathode¹:



Similarly, Na or Zn amalgams in 1 N H₂SO₄ or HClO₄ containing complexing agents such as thiourea yield BiH₃ at the electrode surface⁴:



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1.5.4. by Reaction of Hydrides

1.5.4.1. with Compounds of Nitrogen

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The other alkali-metal hydrides do not react similarly; e.g., LiH with N₂ yields Li₃N

and H_2 . Calcium hydride in alcohol or acetic acid, with $PdCl_2$ or $PtCl_2$ catalysts, reduces $PhNO_2$ to $PhNH_2$.

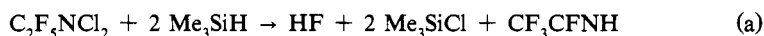
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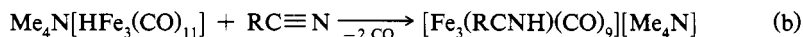
1.5.4.1.2. Involving Covalent Hydrides.

Boranes, alanes, organosilanes and organostannanes are used for reduction of organic nitrogen compounds to compounds containing N—H bonds¹⁻⁴; however, few inorganic systems form by such reactions. The nitrogen chloride $C_2F_5NCl_2$ reacts with Me_3SiH above $-25^\circ C$ to form the fluoroalkylimine⁵:

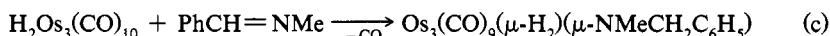


Diborane and N_2F_4 react at $150^\circ C$, yielding a mixture⁶ of NH_3BH_3 , BF_3 , B_5H_9 and H_2 .

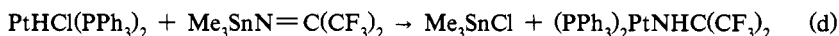
Transition-metal hydrides react with nitrogen compounds to form N—H bond-containing organometallic products¹. The $[HFe_3(CO)_{11}]^-$ cluster anion reacts with nitriles to form a coordinated $RCNH$ species, along with the $RCHN$ -coordinated isomer⁷:



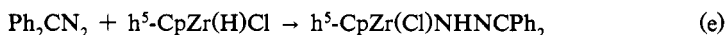
where $R = Me, Ph$. Similar products form in $Re_2(CO)_6(Ph_2PCH_2PPh_2)H_2-MeCN$ reactions⁸. Imines react⁹ with Os:



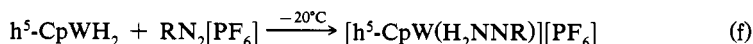
and Pt^{10} hydrides:



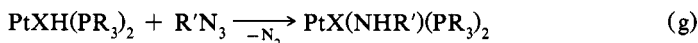
Diazo compounds and diazonium salts⁵ react with Zr:



and W hydrides:



where $R = Ph, p-FC_6H_4, p-MeC_6H_4$. Azide reductions by $PtHX(PR_3)_2$ produce amido complexes in high yield¹⁰:



where $R = Et, Ph$; $X = Cl, N_3, CN$; $R' = Ph, PhCO$.

Nitrogen atoms or radicals form N—H bonds. Nitrogen (4S) atoms, from N_2 dissociation in an electrical discharge, react¹¹ with alkanes to form NH_3 :



and HCN . Nitrogen radicals, $R_2N\cdot$ or $R\dot{N}\cdot$ (triplet) react similarly forming N—H bonds upon H-atom abstraction:

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 35

1.5.4. by Reaction of Hydrides

1.5.4.1. with Compounds of Nitrogen

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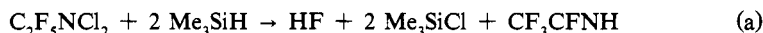
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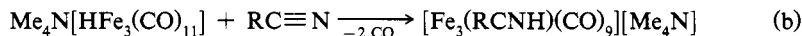
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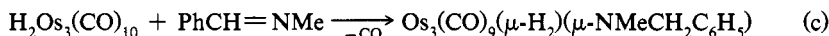


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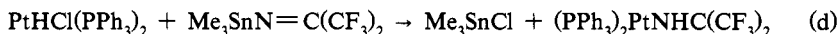
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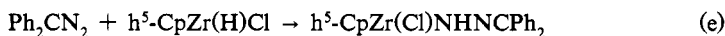
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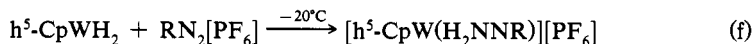
and Pt^{10} hydrides:



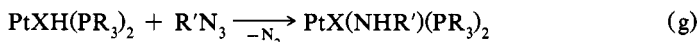
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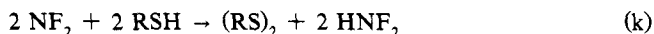
Nitrogen atoms or radicals form N—H bonds. Nitrogen (4S) atoms, from N_2 dissociation in an electrical discharge, react¹¹ with alkanes to form NH_3 :



and HCN . Nitrogen radicals, $R_2N\cdot$ or $R\dot{N}\cdot$ (triplet) react similarly forming N—H bonds upon H-atom abstraction:



Radicals from N_2F_4 dissociation react with thiols to form¹² HNF_2 :

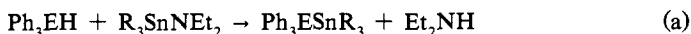


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1.5.4.1.3. Involving Exchange-Cleavage.

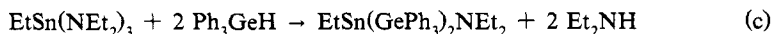
Reactions of amido-group IVB element (Si, Ge, Sn) bonds with group IVB hydrides result in bond cleavage and N—H bond formation¹⁻³, e.g.:



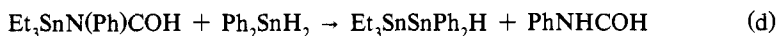
where E = Sn, Ge; R = Et, Ph;



Tris(diethylamino)ethylstannane reacts rapidly with Ph_3GeH cleaving two Sn—N bonds:



but slowly to cleave the third². Cleavage of the Sn—N bond of a stannylamide:



yields the parent phenylformamide⁴. Similar cleavage-exchange reactions involving P—H or As—H and P—N⁵ or Ge—N⁶ bonds:



yield Me_2NH .

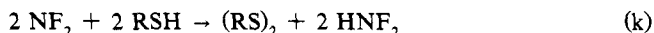
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36 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.4. by Reaction of Hydrides
 1.5.4.1. with Compounds of Nitrogen



Radicals from N_2F_4 dissociation react with thiols to form¹² HNF_2 :

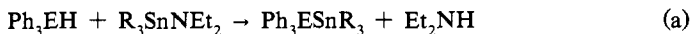


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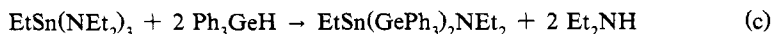
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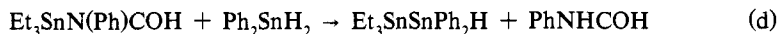
where E = Sn, Ge; R = Et, Ph;



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but slowly to cleave the third². Cleavage of the Sn—N bond of a stannylamide:



yields the parent phenylformamide⁴. Similar cleavage-exchange reactions involving P—H or As—H and P—N⁵ or Ge—N⁶ bonds:



yield Me_2NH .

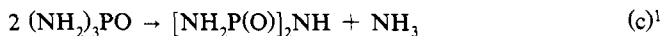
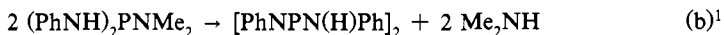
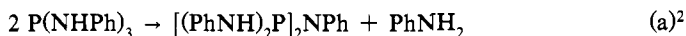
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1.5.4.1.4. Involving Redistribution–Disproportionation.

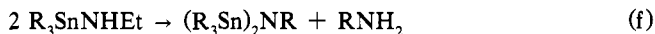
Redistribution produces amines, although the reactions are not often used for amine synthesis. Gem-bis- and tris(amido)P(III) and (V) compounds undergo redistribution with amine elimination, e.g.¹:



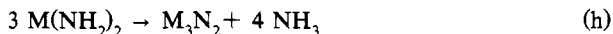
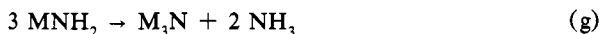
Hydrazine forms from the hydrazinothiophosphinite³ at 80°C:



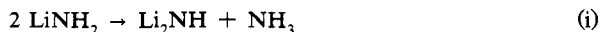
Amidosilanes,⁴ germanes,⁵ and stannanes⁶ react similarly:



where R = Me, Et, n-Bu. Except for NaNH_2 , alkali or alkaline-earth amides eliminate NH_3 on thermolysis:



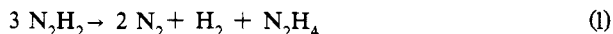
LiNH_2 eliminates NH_3 forming^{7,8} Li_2NH :



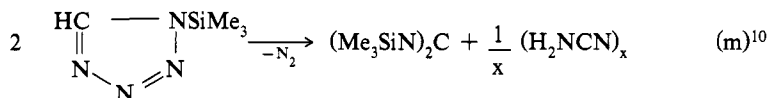
Disproportionation of NH_3 in Ag-zeolite (Ag_{12} -zeolite A) forms the higher hydrides^{8,9}, N_3H_3 , N_3H_4 , N_4H_4 . Normally, disproportionation occurs in the reverse direction. Tetrazene and N_2H_4 disproportionate⁷ to NH_3 and H_2 , faster in the presence of Ni or Pt catalysts:



Diazine disproportionates⁸ above -180°C :



Pyrolysis of the tetraazo ring produces a polymer containing N—H bonds:



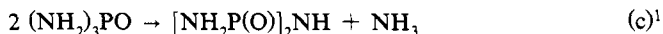
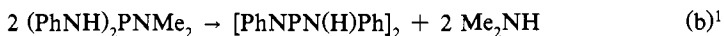
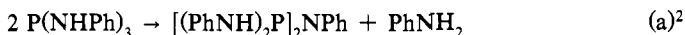
hydrazoic acid¹¹ or NH_2OH ¹², on photolysis:

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 37
 1.5.4. by Reaction of Hydrides
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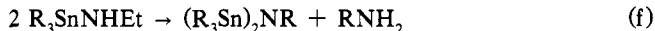
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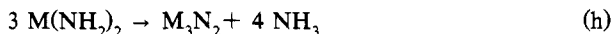
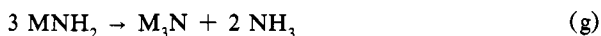
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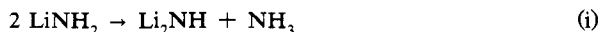
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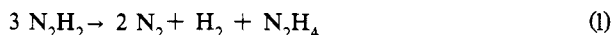
LiNH_2 eliminates NH_3 forming^{7,8} Li_2NH :



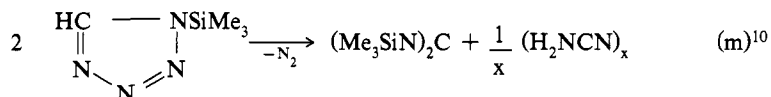
Disproportionation of NH_3 in Ag-zeolite (Ag_{12} -zeolite A) forms the higher hydrides^{8,9}, N_3H_3 , N_3H_5 , N_4H_4 . Normally, disproportionation occurs in the reverse direction. Tetrazene and N_2H_4 disproportionate⁷ to NH_3 and H_2 , faster in the presence of Ni or Pt catalysts:



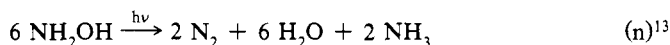
Diazine disproportionates⁸ above -180°C :



Pyrolysis of the tetraazo ring produces a polymer containing N—H bonds:



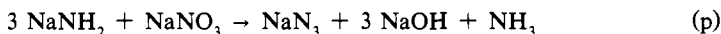
hydrazoic acid¹¹ or NH_2OH ¹², on photolysis:



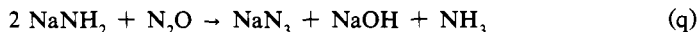
or HN_3 upon thermolysis¹³:



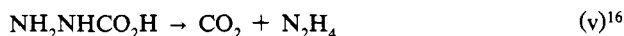
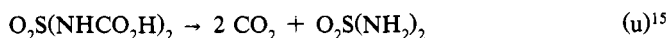
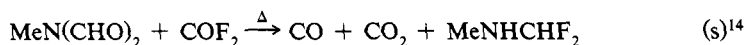
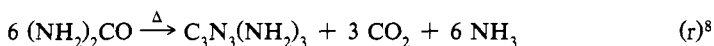
yield NH_3 and N_2 . Heating NaNH_2 with NaNO_3 :



or $\text{N}_2\text{O}(\text{g})$ yields⁸ NH_3 :



Disproportionation with CO_2 elimination can be a ready source of amines:



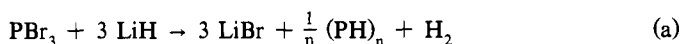
(A.D. NORMAN)

1. E. Fluck, in *Topics in Phosphorus Chemistry*, Vol. 4, M. Grayson, E. J. Griffith, eds., Wiley-Interscience, New York, 1967, p. 291.
2. A. Tarassoli, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.*, **21**, 2684 (1982).
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7. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964. Excellent, brief coverage of basic inorganic nitrogen chemistry.
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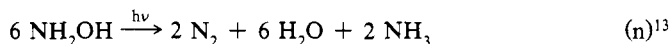
1.5.4.2. with Compounds of Phosphorus

1.5.4.2.1. Involving Ionic Hydrides.

Alkali or alkaline-earth metal hydride reductions of P compounds are less effective than those using complex hydrides, e.g., LiAlH_4 ^{1,2}. Phosphorus tribromide reacts with LiH in Et_2O at 0°C to form a phosphorus subhydride quantitatively³:



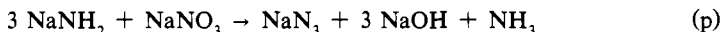
38 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
1.5.4. by Reaction of Hydrides



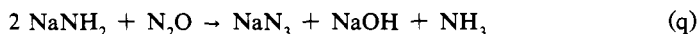
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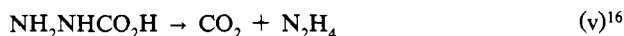
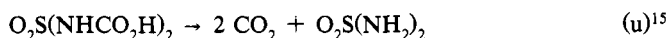
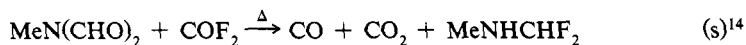
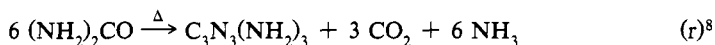
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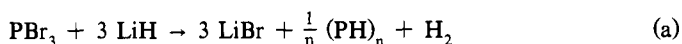
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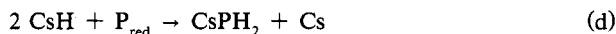
although with PCl_3 low yields of PH_3 are obtained². Similarly, P(O)Br_3 or P(O)Cl_3 react² with LiH , yielding polymeric phosphorus subhydride:



Phosphine forms when PCl_3 vapor in N_2 carrier gas is passed through a column packed with LiH in sand⁴:



Cesium hydride, when heated directly with phosphorus gives¹ CsPH_2 :



Less reactive, alkali-metal hydrides¹ do not react similarly.

Primary and secondary phosphines are produced in low yield upon reaction of LiH with MePCl_2 , and Me_2PCl and PhPCl_2 ².

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1.5.4.2.2. Involving Covalent Hydrides.

Organosilanes and HSiCl_3 reduce selectively halophosphines, phosphonous acids and phosphonic acids and esters¹⁻³. Unlike ionic metal hydrides, organosilanes do not attack C—P bonds. The organosilane reductions usually can be performed without solvents. In addition, they occur with retention of configuration⁴ at the phosphorus.

Silane reductions of phosphorus compounds are listed in Table 1. Mono- or dichlorophosphines and phosphoryl compounds react with Ph_2SiH_2 , e.g.:



TABLE 1. REPRESENTATIVE SILANE REDUCTIONS

Phosphorus compound	Silane ^a	Phosphine	Yield ^a	Ref.
PhPCl_2	$\text{Ph}_2\text{SiH}_2, \text{HSiCl}_3$	PhPH_2	82.75	2
$n\text{-BuP(O)(OEt)}_2$	PMHS^b	$n\text{-BuPH}_2$	90	2
PhP(O)(OEt)_2	Ph_2SiH_2	PhPH_2	87	2
$n\text{-Bu}_2\text{P(O)Cl}$	$\text{Ph}_2\text{SiH}_2, \text{HSiCl}_3$	$n\text{-Bu}_2\text{PH}$	95.63	5,6
$n\text{-BuPhP(O)Cl}$	HSiCl_3	$n\text{-BuPhPH}$	60	6
$(m\text{-MeC}_6\text{H}_4)_2\text{P(O)Cl}$	HSiCl_3	$m\text{-MeC}_6\text{H}_4\text{PH}_2$	31	6
Ph_2PCl	$\text{Ph}_2\text{SiH}_2, \text{HSiCl}_3$	Ph_2PH	59.75	5

^a Yields are for the respective silanes, as listed.

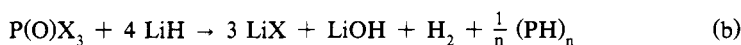
^b PMHS = polymethylhydrosilane, $\text{Me}_3\text{SiO}[\text{SiH}(\text{Me})\text{O}]_x\text{OSiMe}_3$.

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 39

1.5.4. by Reaction of Hydrides

1.5.4.2. with Compounds of Phosphorus

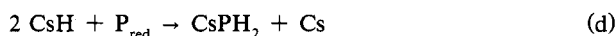
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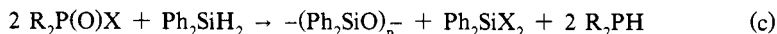
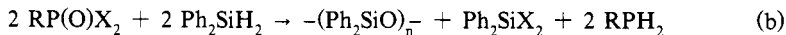


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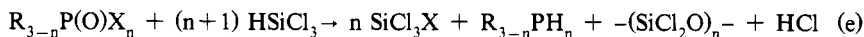
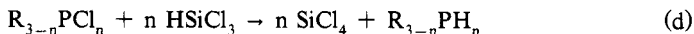
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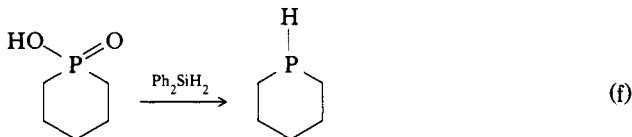
^b $\text{PMHS} = \text{polymethylhydrosilane}, \text{Me}_3\text{SiO}[\text{SiH}(\text{Me})\text{O}]_x\text{OSiMe}_3$.



where $n = 1-3$; $\text{X} = \text{OH}, \text{Cl}, \text{alkoxy}$; $\text{R} = \text{alkyl}, \text{aryl}$. Reactions proceed smoothly in neat silane at $200-275^\circ\text{C}$. Similarly, HSiCl_3 reductions are performed in refluxing benzene:

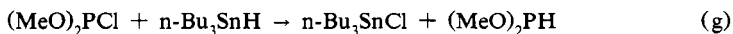


where $n = 1, 2$; $\text{X} = \text{Cl}, \text{OH}, \text{alkoxy}$; $\text{R} = \text{alkyl}, \text{aryl}$. These reactions are run in the presence of a tertiary amine, (e.g., Et_3N , pyridine) which scavenges HCl from the reaction medium. Phosphinic acid chlorides are reduced by arylsilanes more efficiently than are the free acids or their esters. Organosilane reduction of cyclic phosphorus moieties occurs effectively with minimal ring cleavage³. Phosphorinane is obtained in 60% yield by reaction of Ph_2SiH_2 at 200°C with the cyclic phosphinic acid⁷:

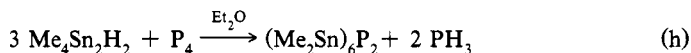


Bicyclic and tricyclic phosphines³, e.g., $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{PH}$, are formed equally well.

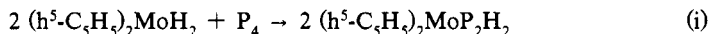
Tri-*n*-butylstannane reacts smoothly with $(\text{MeO})_2\text{PCl}$ at 25°C forming $(\text{MeO})_2\text{PH}$ along with traces⁸ of P(OMe)_3 and PH_3 :



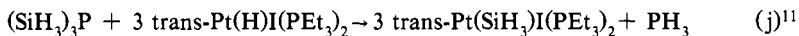
but the analogous reaction with MeOPCl_2 does not occur. Tetramethyldistannane reacts with P_4 at 0°C in the dark to form⁹ PH_3 :



Transition-metal hydride reactions can result in P-H bond formation. White phosphorus and $(\text{h}^5\text{-C}_3\text{H}_5)_2\text{MoH}_2$ yield the metal-coordinated¹⁰ P_2H_2 :



Phosphine results from the Pt hydride complex cleavage of $(\text{SiH}_3)_3\text{P}$.



Elemental phosphorus with covalent hydrides can be converted to phosphines. White phosphorus when passed through a silent electric discharge in the presence of C_2H_4 , C_3H_8 , CH_4 , NH_3 or N_2H_4 , yields traces¹² of PH_3 . Reaction with LiPH_2 produces PH_3 in 95% yield¹³:



and reaction with alkenes in the presence of O_2 forms β -hydroxyphosphinic acids¹⁴:



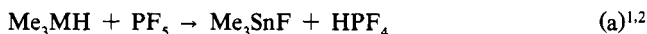
Passage of PH_3 , $\text{PH}_3\text{-SiH}_4$ or $\text{PH}_3\text{-GeH}_4$ through a silent electric discharge or hot-tube pyrolysis reactor results in complex product mixtures, which involve formation of new P—H bonds. Major products from PH_3 , $\text{PH}_3\text{-SiH}_4$, or $\text{PH}_3\text{-GeH}_4$ reactions include P_2H_4 , SiH_3PH_2 and GeH_3PH_2 , in addition to Si_2H_6 and Ge_2H_6 . Lesser products include^{15,16} $\text{Si}_2\text{H}_5\text{PH}_2$, $(\text{SiH}_3)_2\text{PH}$, Si_3H_8 , Si_4H_{10} , $(\text{GeH}_3)_2\text{PH}$, and Ge_3H_8 .

(A.D. NORMAN)

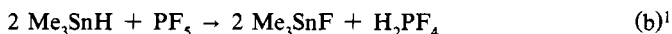
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2. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
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4. K. Marsi, *J. Org. Chem.*, **39**, 265 (1974).
5. H. Fritzsche, U. Hasserodt, F. Korte, *Chem. Ber.*, **98**, 1681 (1965).
6. H. Fritzsche, U. Hasserodt, F. Korte, U.S. Pat. 3,261,871 (1966); *Chem. Abstr.*, **65**, 18,619 (1966).
7. J. B. Lambert, W. L. Oliver, Jr., *Tetrahedron*, **27**, 4245 (1971).
8. L. Centofanti, *Inorg. Chem.*, **12**, 1131 (1973).
9. M. Dräger, B. Mathiasch, *Angew. Chem., Int. Ed. Engl.*, **20**, 1029 (1981).
10. J. C. Green, M. L. H. Green, G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 212 (1974).
11. E. A. V. Ebsworth, J. M. Edward, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1673 (1976).
12. E. R. Zabolatny, H. Gesser, *J. Am. Chem. Soc.*, **81**, 6091 (1959).
13. S. Baudler, *Angew. Chem., Int. Ed. Engl.*, **21**, 492 (1982).
14. A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).
15. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
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1.5.4.2.3. Involving Exchange-Cleavage.

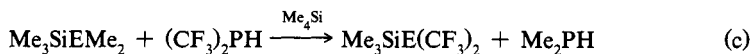
Phosphorus-hydrogen bonds form in intermolecular exchange. Trimethylstannane or Me_3SiH with PF_5 reacts:



where M = Si, Sn;



Reactions at 25°C between $\text{Me}_3\text{SiPMe}_2$ or $\text{Me}_3\text{SiAsMe}_2$ and $(\text{CF}_3)_2\text{PH}$ yield³ Me_2PH :



where E = P, As.

(A.D. NORMAN)

1. P. M. Treichel, R. A. Goodrich, S. B. Pierce, *J. Am. Chem. Soc.*, **89**, 2017 (1967).
2. A. H. Cowley, R. W. Braun, *Inorg. Chem.*, **12**, 491 (1973).
3. J. E. Byrne, C. R. Russ, *J. Inorg. Nucl. Chem.*, **36**, 35 (1974).

1.5.4.2.4. Involving Redistribution-Disproportionation.

Disproportionation of P—P bond-containing phosphines can produce new P—H bonds^{1,2}. Gaseous P_2H_4 in a hot-cold reactor³ or neat liq P_2H_4 at 4° 30–40°C reacts to form PH_3 , P_3H_5 :



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 41
 1.5.4. by Reaction of Hydrides
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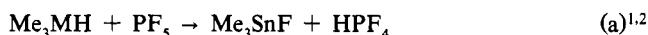
Passage of PH_3 , $\text{PH}_3\text{-SiH}_4$ or $\text{PH}_3\text{-GeH}_4$ through a silent electric discharge or hot-tube pyrolysis reactor results in complex product mixtures, which involve formation of new P—H bonds. Major products from PH_3 , $\text{PH}_3\text{-SiH}_4$, or $\text{PH}_3\text{-GeH}_4$ reactions include P_2H_4 , SiH_3PH_2 and GeH_3PH_2 , in addition to Si_2H_6 and Ge_2H_6 . Lesser products include^{15,16} $\text{Si}_2\text{H}_5\text{PH}_2$, $(\text{SiH}_3)_2\text{PH}$, Si_3H_8 , Si_4H_{10} , $(\text{GeH}_3)_2\text{PH}$, and Ge_3H_8 .

(A.D. NORMAN)

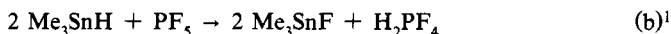
1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
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4. K. Marsi, *J. Org. Chem.*, 39, 265 (1974).
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15. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
16. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.* 4, 1 (1968).

1.5.4.2.3. Involving Exchange-Cleavage.

Phosphorus-hydrogen bonds form in intermolecular exchange. Trimethylstannane or Me_3SiH with PF_5 reacts:



where M = Si, Sn;



Reactions at 25°C between $\text{Me}_3\text{SiPMe}_2$ or $\text{Me}_3\text{SiAsMe}_2$ and $(\text{CF}_3)_2\text{PH}$ yield³ Me_2PH :



where E = P, As.

(A.D. NORMAN)

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2. A. H. Cowley, R. W. Braun, *Inorg. Chem.*, 12, 491 (1973).
3. J. E. Byrne, C. R. Russ, *J. Inorg. Nucl. Chem.*, 36, 35 (1974).

1.5.4.2.4. Involving Redistribution-Disproportionation.

Disproportionation of P—P bond-containing phosphines can produce new P—H bonds^{1,2}. Gaseous P_2H_4 in a hot-cold reactor³ or neat liq P_2H_4 at 4° 30–40°C reacts to form PH_3 , P_3H_5 :



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 41
 1.5.4. by Reaction of Hydrides
 1.5.4.2. with Compounds of Phosphorus

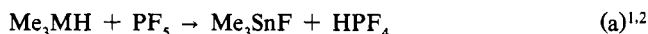
Passage of PH_3 , $\text{PH}_3\text{-SiH}_4$ or $\text{PH}_3\text{-GeH}_4$ through a silent electric discharge or hot-tube pyrolysis reactor results in complex product mixtures, which involve formation of new P—H bonds. Major products from PH_3 , $\text{PH}_3\text{-SiH}_4$, or $\text{PH}_3\text{-GeH}_4$ reactions include P_2H_4 , SiH_3PH_2 and GeH_3PH_2 , in addition to Si_2H_6 and Ge_2H_6 . Lesser products include^{15,16} $\text{Si}_2\text{H}_5\text{PH}_2$, $(\text{SiH}_3)_2\text{PH}$, Si_3H_8 , Si_4H_{10} , $(\text{GeH}_3)_2\text{PH}$, and Ge_3H_8 .

(A.D. NORMAN)

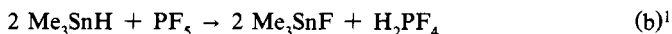
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7. J. B. Lambert, W. L. Oliver, Jr., *Tetrahedron*, **27**, 4245 (1971).
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14. A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).
15. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
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1.5.4.2.3. Involving Exchange-Cleavage.

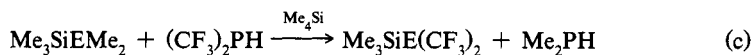
Phosphorus-hydrogen bonds form in intermolecular exchange. Trimethylstannane or Me_3SiH with PF_5 reacts:



where M = Si, Sn;



Reactions at 25°C between $\text{Me}_3\text{SiPMe}_2$ or $\text{Me}_3\text{SiAsMe}_2$ and $(\text{CF}_3)_2\text{PH}$ yield³ Me_2PH :



where E = P, As.

(A.D. NORMAN)

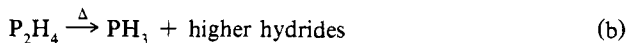
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1.5.4.2.4. Involving Redistribution-Disproportionation.

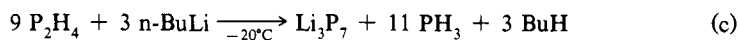
Disproportionation of P—P bond-containing phosphines can produce new P—H bonds^{1,2}. Gaseous P_2H_4 in a hot-cold reactor³ or neat liq P_2H_4 at 4 30–40°C reacts to form PH_3 , P_3H_5 :



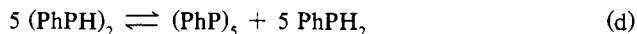
and the higher mol wt phosphorus subhydrides $P_n H_{n+2}$, $P_n H_n$, $P_n H_{n-2}$ etc.:



Diphosphine and n-BuLi react in THF to form⁴ PH_3 :



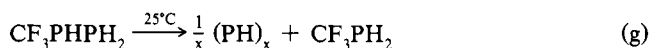
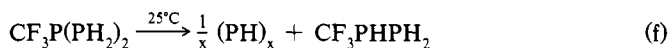
Phenylphosphine and $(PhP)_5$ in solution exist in equilibrium with⁵ $(PhPH)_2$:



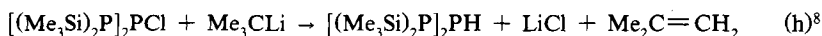
Mono- and bis(borane)diphosphines at 174°C and 130°C, respectively, undergo thermolysis to form Me_2PHBH_3 :



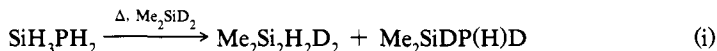
and trimeric or tetrameric $(BH_2PMe_2)_x$ polymers⁹. The triphosphine $CF_3P(PH_2)_2$ disproportionates stepwise, yielding di- and monophosphine products⁷:



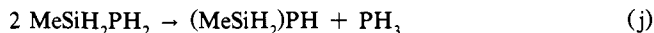
β -Hydrogen elimination from the product of Me_3Cl reaction with $[(Me_3Si)_2P]_2PCl$ yields a triphosphine:



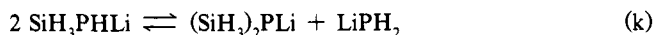
The cyclotriphosphine $(t\text{-BuP})_3PH$ disproportionates to mono-, di- and tetraphosphines⁴. Thermolysis of SiH_3PH_2 at 400°C yields PH_3 in addition to SiH_4 , H_2 and solid polymeric subhydrides². Under controlled conditions at 210°C, PH_3 , in addition to Si_2H_6 , SiH_3PH_2 and Si_3PH_9 , forms in the decomposition of $Si_2H_5PH_2$. Pyrolysis of SiH_3PH_2 in the presence of Me_2SiD_2 yields $Me_2Si_2H_2D_2$ and $Me_2SiDP(H)D$:



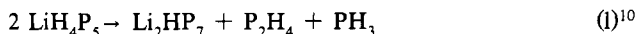
in a 2.6:1 ratio, the latter product containing a P—D bond formed through P—H insertion in a Si—D bond of⁹ Me_2SiD_2 . In the presence of LiOEt methylsilylphosphine redistributes spontaneously¹⁰:



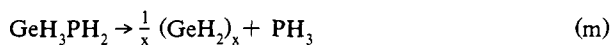
Lithiated silylphosphine¹⁰ equilibrates with $LiPH_2$ and $(SiH_3)_2PLi$:

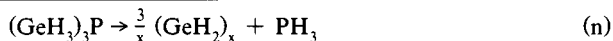


Above $-30^\circ C$ lithiocyclopentaphosphine disproportionates:



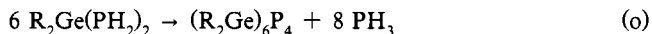
At 25°C in the presence of H_2O catalyst, germylphosphine and $(GeH_3)_3P$ yield PH_3 and $(GeH_2)_x$:





The $(\text{GeH}_2)_x$, being unstable, decomposes^{1,2} to $(\text{GeH})_x$, GeH_4 , traces of higher germanes and H_2 . Silylphosphine^{1,2} or $\text{Si}_2\text{H}_5\text{PH}_2$ ² react below -78°C when coordinated to BF_3 . Phosphine is produced quantitatively.

Alkyl(phosphino)germanes with H_3PO_3 catalyst present eliminate PH_3 upon redistribution as more highly condensed germylphosphines are formed¹¹.



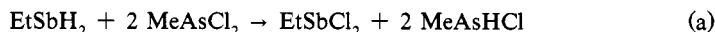
where $\text{R} = \text{Me, Et}$.

(A.D. NORMAN)

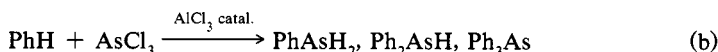
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1.5.4.3. with Compounds of Arsenic.

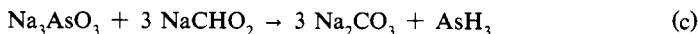
Several hydride reactions lead to As—H bonds; however, these are not preferred routes¹. Ethylstibine and MeAsCl_2 react at 25°C to form² MeAsHCl :



Benzene, in the presence of AlCl_3 catalyst and $i\text{-C}_5\text{H}_{12}$, reacts with AsCl_3 to form phenylarsines³:



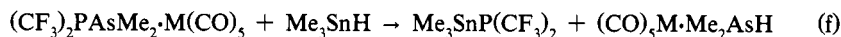
Reaction stoichiometry is not established. Thermolysis at 400°C of an Na arsenite-Na formate mixture yields⁴ AsH_3 :



Dimethylphosphine cleavage of the As—As bond in $(\text{CF}_3)_4\text{As}_2$:



or Me_3SnH cleavage of As—As or As—P bonds in the metal-coordinated analogues⁶

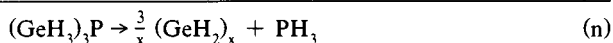


where $\text{M} = \text{Cr, Mo}$, produce metal-coordinated Me_2AsH .

Arsine redistribution reactions yield compounds containing new As—H bonds. Germylarsine in the presence of B_2H_6 or H_2O or SiH_3AsH_2 with B_2H_6 produce AsH_3 quantitatively⁷:

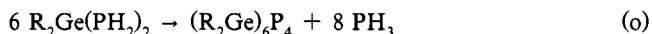
1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 43

1.5.4. by Reaction of Hydrides



The $(\text{GeH}_2)_x$, being unstable, decomposes^{1,2} to $(\text{GeH})_x$, GeH_4 , traces of higher germanes and H_2 . Silylphosphine^{1,2} or $\text{Si}_2\text{H}_5\text{PH}_2$ react below -78°C when coordinated to BF_3 . Phosphine is produced quantitatively.

Alkyl(phosphino)germanes with H_3PO_3 catalyst present eliminate PH_3 upon redistribution as more highly condensed germylphosphines are formed¹¹.



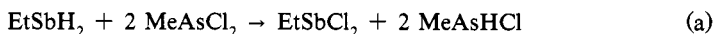
where $\text{R} = \text{Me, Et}$.

(A.D. NORMAN)

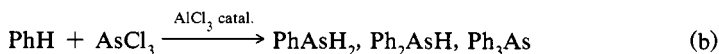
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1.5.4.3. with Compounds of Arsenic.

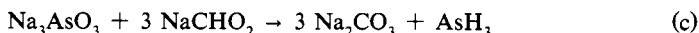
Several hydride reactions lead to As—H bonds; however, these are not preferred routes¹. Ethylstibine and MeAsCl_2 react at 25°C to form² MeAsHCl :



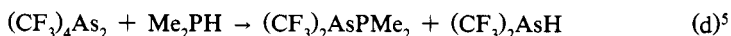
Benzene, in the presence of AlCl_3 catalyst and $i\text{-C}_5\text{H}_{12}$, reacts with AsCl_3 to form phenylarsines³:



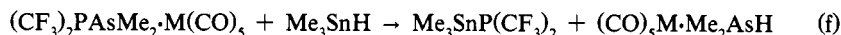
Reaction stoichiometry is not established. Thermolysis at 400°C of an Na arsenite–Na formate mixture yields⁴ AsH_3 :



Dimethylphosphine cleavage of the As—As bond in $(\text{CF}_3)_4\text{As}_2$:

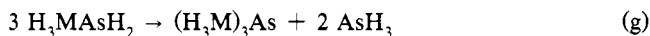


or Me_3SnH cleavage of As—As or As—P bonds in the metal-coordinated analogues⁶

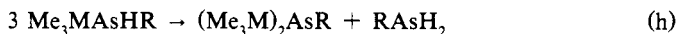


where $\text{M} = \text{Cr, Mo}$, produce metal-coordinated Me_2AsH .

Arsine redistribution reactions yield compounds containing new As—H bonds. Germylarsine in the presence of B_2H_6 or H_2O or SiH_3AsH_2 with B_2H_6 produce AsH_3 quantitatively⁷:



where M = Si, Ge. However, H_2O cleavage of Ge—As bonds is not fast, as is the case with Si—As bonds⁷. Similarly, unsymmetrically substituted silyl- and germyl-arsines redistribute readily⁸:

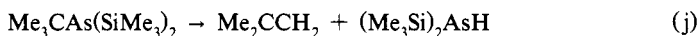


where M = Si, Ge; M = Me, Ph.

Hydride transfer in the decomposition of $\text{CF}_3\text{As}(\text{PH}_2)_2$ yields⁹ CF_3AsH_2 :



β -Hydrogen transfer during thermolysis¹⁰ of $\text{Me}_3\text{CAs}(\text{SiMe}_3)_2$ results in $(\text{Me}_3\text{Si})_2\text{AsH}$:



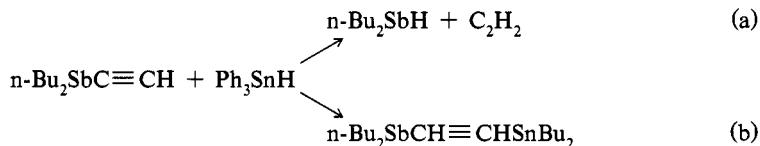
The decomposition of AsH_3 , AsH_3 — SiH_4 or AsH_3 — GeH_4 mixtures in ozonizer discharge reactions yields products that are the result of AsH , SiH_2 or GeH_2 insertion into As—H bonds. Major As—H bond-containing products are^{7,11} As_2H_4 , SiH_3AsH_2 and GeH_3AsH_2 .

(A.D. NORMAN)

1. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
2. P. Chaudhury, M. F. El-Shazley, C. Spring, A. Rheingold, *Inorg. Chem.*, **18**, 543 (1979).
3. L. Schmerling, U.S. Pat. 2,842,579 (1958); *Chem. Abstr.* **55**, 497 (1961).
4. D. T. Hurd, *Chemistry of the Hydrides*, John Wiley and Sons, New York, 1952.
5. R. G. Cavell, R. C. Dobbie, *J. Chem. Soc., A*, 1406 (1968).
6. J. Grobe, D. LeVan, *Z. Naturforsch., Teil B*, **36**, 666 (1981).
7. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
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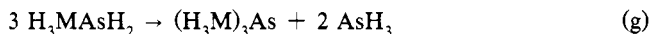
1.5.4.4. with Compounds of Antimony.

Examples of Sb—H bond formation by reactions of Sb compounds with either covalent or ionic binary hydrides are rare¹. The alkynlstibine, $n\text{-Bu}_2\text{SbC}\equiv\text{CH}$, reacts with Ph_3SnH , where instead of hydrostannylation of the alkyne bond, tin hydride cleavage of the Sb—C bond:

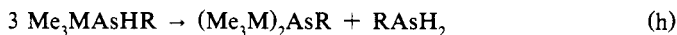


leads to $n\text{-Bu}_2\text{SbH}$ and acetylene². The generality of this reaction for R_2SbH synthesis is not tested. The germane, $n\text{-Bu}_3\text{GeH}$, reacts with $n\text{-Bu}_2\text{SbC}\equiv\text{CH}$ to form $n\text{-Bu}_3\text{GeC}\equiv\text{CH}$ and $n\text{-Bu}_2\text{SbCHCHSbBu}_2$, as a result of $n\text{-Bu}_2\text{SbH}$ intermediate formation²:

44 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
1.5.4. by Reaction of Hydrides



where M = Si, Ge. However, H_2O cleavage of Ge—As bonds is not fast, as is the case with Si—As bonds⁷. Similarly, unsymmetrically substituted silyl- and germyl-arsines redistribute readily⁸:

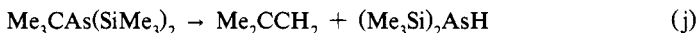


where M = Si, Ge; M = Me, Ph.

Hydride transfer in the decomposition of $\text{CF}_3\text{As}(\text{PH}_2)_2$ yields⁹ CF_3AsH_2 :



β -Hydrogen transfer during thermolysis¹⁰ of $\text{Me}_3\text{CAs}(\text{SiMe}_3)_2$ results in $(\text{Me}_3\text{Si})_2\text{AsH}$:



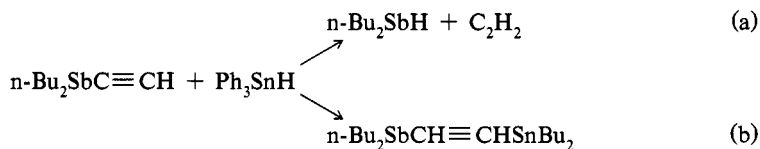
The decomposition of AsH_3 , AsH_3 — SiH_4 or AsH_3 — GeH_4 mixtures in ozonizer discharge reactions yields products that are the result of AsH , SiH_2 or GeH_2 insertion into As—H bonds. Major As—H bond-containing products are^{7,11} As_2H_4 , SiH_3AsH_2 and GeH_3AsH_2 .

(A.D. NORMAN)

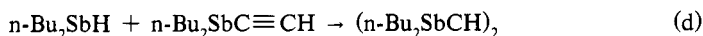
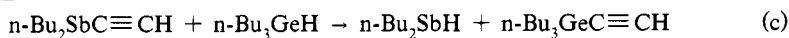
1. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
2. P. Chaudhury, M. F. El-Shazley, C. Spring, A. Rheingold, *Inorg. Chem.*, **18**, 543 (1979).
3. L. Schmerling, U.S. Pat. 2,842,579 (1958); *Chem. Abstr.* **55**, 497 (1961).
4. D. T. Hurd, *Chemistry of the Hydrides*, John Wiley and Sons, New York, 1952.
5. R. G. Cavell, R. C. Dobbie, *J. Chem. Soc., A*, 1406 (1968).
6. J. Grobe, D. LeVan, *Z. Naturforsch., Teil B*, **36**, 666 (1981).
7. J. E. Drake, C. Riddle, *Q. Rev. Chem. Soc.*, 263 (1970).
8. J. W. Drake, J. E. Anderson, *J. Inorg. Nucl. Chem.*, **35**, 1032 (1973).
9. R. Demuth, J. Grobe, *Z. Naturforsch., Teil B*, **28**, 219 (1973).
10. G. Becker, G. Gutenkunst, H. J. Wessely, *Z. Anorg. Allg. Chem.*, **462**, 113 (1980).
11. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).

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Reactions of bismuth compounds with hydrides to form Bi—M-containing compounds are not known^{1,2}.

(A.D. NORMAN)

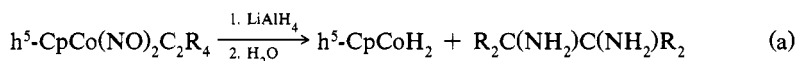
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1.5.5. by Reaction of Complex Hydrides

1.5.5.1. with Compounds of Nitrogen.

Complex metal hydroborates, hydroaluminates, hydridoferrates and modified complex hydrides (e.g., $\text{NaBH}_4\text{--AlCl}_3$) are used extensively in syntheses of organic compounds containing N—H bonds¹⁻⁵, but few inorganic or organometallic N—H bonds are prepared this way.

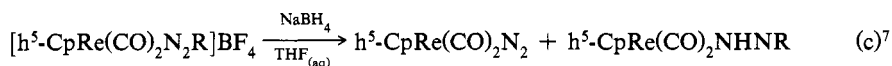
Reaction of $\text{h}^5\text{-CpCo}$ -coordinated nitroso compounds with LiAlH_4 in THF followed by treatment with H_2O produces diamine products in 90% yield⁶:



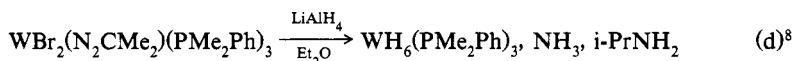
where R = H, Me, Et. Magnesium-bonded imines, formed from RMgX reaction with nitriles, are reduced by LiAlH_4 to primary amines:



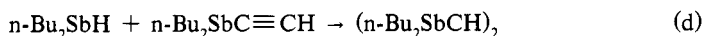
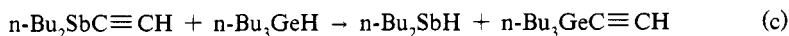
Transition-metal-coordinated N_2R complexes react with complex hydrides to form NHNHNR complexes or free NH_3 or amines in reactions whose stoichiometries are not established:



where R = *p*- MeC_6H_4 , *o*- $\text{CF}_3\text{C}_6\text{H}_4$, *p*- MeC_6H_4 ;



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 45



(A.D. NORMAN)

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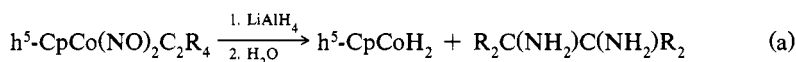
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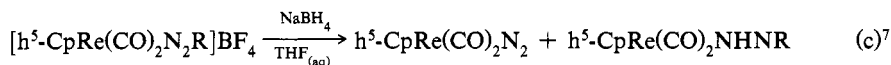
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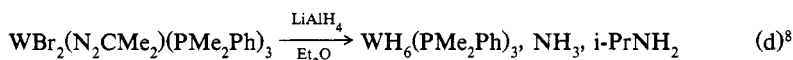
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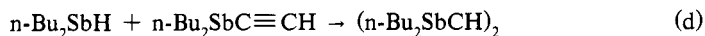
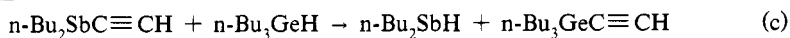
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(A.D. NORMAN)

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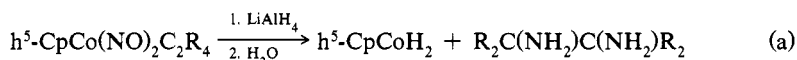
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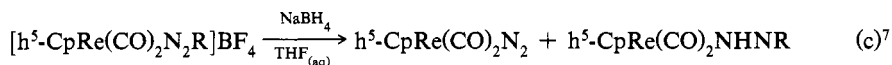
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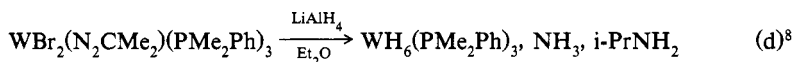
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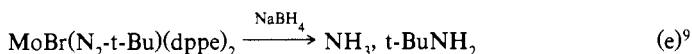


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where dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. These reactions produce NH_3 and primary amines in high yields.

Complex hydride reductions of N_2 , N_2O , $[\text{CN}]^-$ and nitriles in reactions containing complex mixtures of metal-ion species produce N—H bonded products^{10,11} by reactions that may relate to those of the biological nitrogenases¹¹. Complete reaction stoichiometries are not well established. These reactions are not competitive with other methods for NH_3 or amine synthesis. Nitrogen reacts in H_2O with a mixture of NaBH_4 , S-donor ligands (e.g., $\text{NH}_2\text{C}_2\text{H}_4\text{SH}$) and Mo and Fe salts to form NH_3 and N_2H_4 in low yield¹⁰. In similar systems, nitriles and isonitriles are reduced to NH_3 and amines in low yield¹⁰.

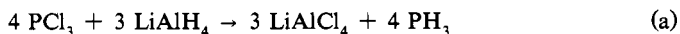
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6. P. N. Becker, M. A. White, R. G. Bergman, *J. Am. Chem. Soc.*, **102**, 5676 (1980).
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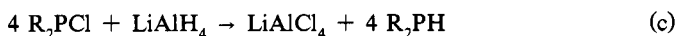
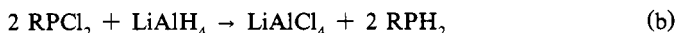
1.5.5.2. with Compounds of Phosphorus

1.5.5.2.1. Involving Halides.

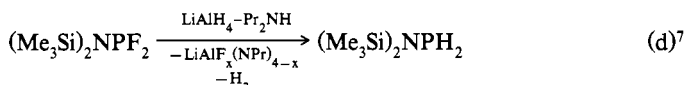
Lithium tetrahydroaluminate reduction of phosphorus halides is a route to PH_3 and primary and secondary phosphines¹⁻³. Phosphorus trichloride at -115°C in Me_2O is reduced to PH_3 in 79% yield:



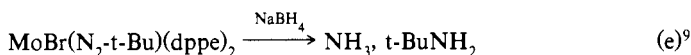
Under similar conditions, LiAlH_4 reaction with $\text{P}(\text{O})\text{Cl}_3$ at -115°C yields⁴ PH_3 . Mono- and dichlorophosphorus(III) compounds are reduced in ether (Me_2O , Et_2O , THF, glymes) to the corresponding secondary and primary phosphines:



e.g., MePH_2 , 55% yield⁵; PhPH_2 , 75% yield³ and Ph_2PH , 70% yield⁶. Reaction of Ph_2PCl_3 with LiAlH_4 yields² Ph_2PH , but no Ph_2PH_3 . The fluoroaminophosphine, $(\text{Me}_3\text{Si})_2\text{NPF}_2$, is reduced by a LiAlH_4 -secondary amine mixture:



46 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
1.5.5. by Reaction of Complex Hydrides



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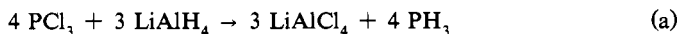
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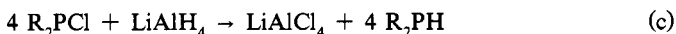
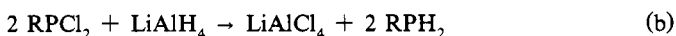
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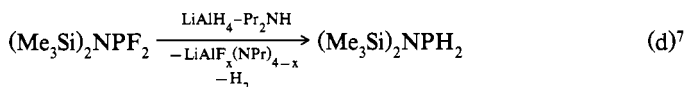
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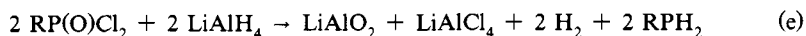
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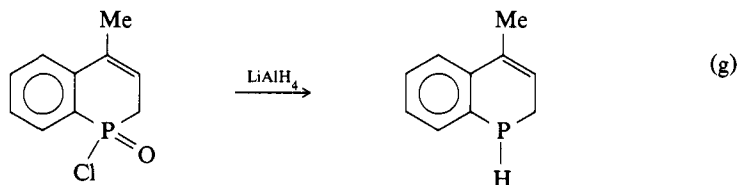
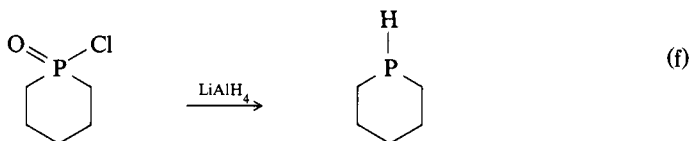
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Phosphonyl dichlorides react with LiAlH_4 forming mono- and bis(phosphino)-substituted products. From PhP(O)Cl_2 reduction, PhPH_2 is obtained³:

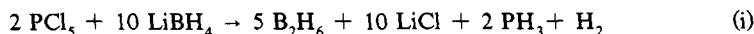
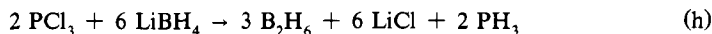


and from $\text{RR'C[P(O)Cl}_2\text{]}_2$ compounds, phosphines such as $\text{H}_2\text{C(PH}_2\text{)}_2$, $\text{Me}_2\text{C(PH}_2\text{)}_2$ and $(\text{n-Bu})_2\text{C(PH}_2\text{)}_2$ form⁸. Diphenylphosphine is formed³ in 93% yield by LiAlH_4 reduction of $\text{Ph}_2\text{P(O)Cl}$. Reduction of phosphinic chlorides yields the cyclic secondary phosphines^{3,9}:



The substituted Na hydroaluminates, $\text{Na}[(\text{MeOCH}_2\text{CH}_2\text{O})_2\text{AlH}_2]$, reacts with Ph_2PCl , forming Ph_2PH along with the undesired alkylation-cleavage products¹⁰ MePh_2P and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OH}$.

Alkali-metal tetrahydaborate reduction of phosphorus halides is of limited utility^{1,3}. Lithium tetrahydaborate reaction with PCl_3 or PCl_5 in Et_2O at -80°C produces PH_3 , but yields are low¹¹:



Reactions of R_2PCl or RPCl_2 with LiBH_4 yield only the borane-coordinated phosphine products¹¹.

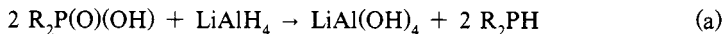
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1. L. Maier, *Prog. Inorg. Chem.*, 5, 27 (1963).
2. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
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4. E. Wiberg, G. Müller-Schiedmayer, *Z. Anorg. Allg. Chem.*, 308, 352 (1961).
5. L. J. Malone, R. W. Parry, *Inorg. Chem.*, 6, 176 (1967).
6. W. Kuchen, H. Buchwald, *Chem. Ber.*, 91, 2871 (1958).
7. E. Niecke, R. Rüger, *Angew. Chem., Int. Ed. Engl.*, 21, 62 (1982).
8. H. R. Hays, T. J. Logan, *J. Org. Chem.*, 31, 339 (1966).
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10. M. Gallagher, G. Pollard, *Phosphorus*, 6, 61 (1975).
11. B. D. James, M. G. H. Wallbridge, *Prog. Inorg. Chem.*, 11, 99 (1970).

- 48 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.5. by Reaction of Complex Hydrides
 1.5.5.2. with Compounds of Phosphorus

1.5.5.2. Involving Oxygen Compounds.

Primary and secondary phosphines are prepared by LiAlH_4 reduction of organophosphorus acids, or esters¹⁻³. Reactions of phosphoryl halides are described in §1.5.5.2.1. Phosphinic acids:



phosphinate esters:



phosphonous acids:

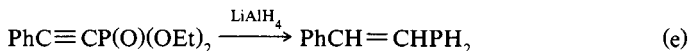


phosphonate esters:



are reduced to phosphines. These reactions often allow syntheses of complex phosphines that cannot be obtained easily by other methods. Phosphines that can be prepared by this method are listed in Table 1. Reactions are carried out under N_2 in ether at or below RT. After reduction, aq acid is added to hydrolyze intermediate aluminophosphorus species, e.g., $[\text{Al}(\text{PPh}_2)_4]^-$ in the $\text{Ph}_2\text{P}(\text{O})(\text{OEt})$ reduction¹.

Reaction of an alkynylphosphonate with LiAlH_4 reduces both the alkyne and the phosphoryl groups⁹:



Phosphoramides react variously with LiAlH_4 . Phosphoryl reduction and P—N bond cleavage can occur as¹:

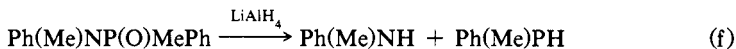
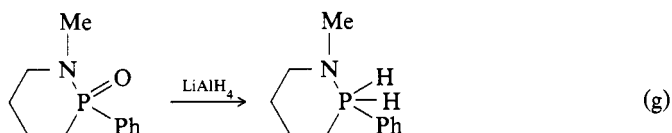


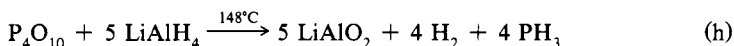
TABLE 1. PHOSPHONATE OR PHOSPHINATE REDUCTIONS

Reactant	Product	Yield (%)	Ref.
$\text{MeP}(\text{O})(\text{OMe})_2$	MePH_2	87	4
$\text{EtP}(\text{O})(\text{OEt})_2$	EtPH_2	65	1
$\text{PhP}(\text{O})(\text{OH})_2$	PhPH_2	13	3
$\text{PhP}(\text{O})(\text{OEt})_2$	PhPH_2	62	3
$\text{PhCH}_2\text{P}(\text{O})(\text{OEt})_2$	PhCH_2PH_2	48	1,3
$\text{PhP}(\text{H})\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$	$\text{PhP}(\text{H})\text{CH}_2\text{PH}_2$	30	5
$\text{o-NH}_2\text{C}_6\text{H}_4\text{P}(\text{O})(\text{OEt})_2$	$\text{o-NH}_2\text{C}_6\text{H}_4\text{PH}_2$	85	6
$(\text{EtO})_2\text{P}(\text{O})(\text{CH}_2)_3\text{P}(\text{O})(\text{OEt})_2$	$\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2$	57	7
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$	$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PH}_2$	21	8
$\text{PhP}[\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2]_2$	$\text{PhP}(\text{CH}_2\text{CH}_2\text{PH}_2)_2$	55	8
$\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2]_3$	$\text{P}(\text{CH}_2\text{CH}_2\text{PH}_2)_3$	28	8
$\text{Ph}_2\text{P}(\text{O})\text{OH}$	Ph_2PH	80	1
$(\text{C}_6\text{H}_{11})_2\text{P}(\text{O})\text{OH}$	$(\text{C}_6\text{H}_{11})_2\text{PH}$	50	1
$\text{Me}_3\text{SnCH}_2\text{P}(\text{O})(\text{Ph})(\text{OEt})$	$\text{Me}_3\text{SnCH}_2\text{P}(\text{H})\text{Ph}$	48	5

In contrast, an analogous cyclic compound is reduced without P—N bond cleavage¹:



When heated with a deficit of LiAlH_4 , solid powdered P_4O_{10} produces¹⁰ small quantities of PH_3 :



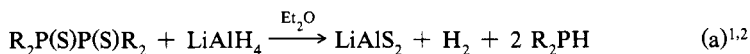
Metal phosphites in H_2O are reduced in low yield¹¹ to PH_3 .

(A.D. NORMAN)

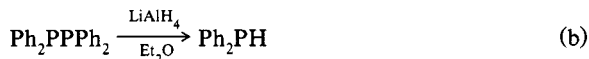
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1.5.5.2.3. Involving Other Derivatives.

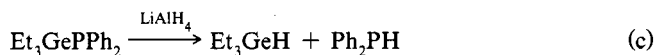
Cleavage of diphosphines with LiAlH_4 can be a route to secondary phosphines, e.g., diphosphine disulfides react:



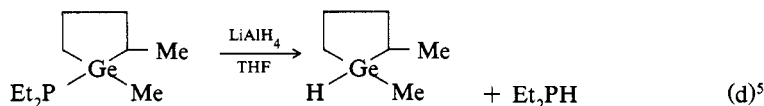
where $\text{R} = \text{Me}$, Et , CH_2Ph , $n\text{-Bu}$, C_6H_{11} , Ph . Yields range from 68 to 80%. Because $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ is readily available, the reaction is good for preparing large quantities² (50–400 mmol) of Me_2PH . Tetraphenyldiphosphine is reduced³ to Ph_2PH :



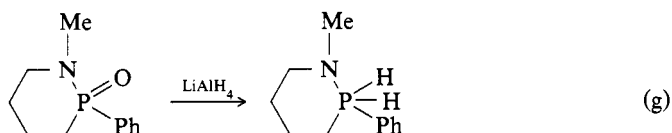
Germanium–P bond cleavage by LiAlH_4 yields⁴ Ph_2PH :



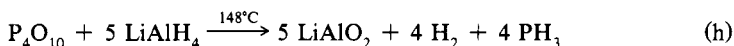
or⁵ Et_2PH :



In contrast, an analogous cyclic compound is reduced without P—N bond cleavage¹:



When heated with a deficit of LiAlH_4 , solid powdered P_4O_{10} produces¹⁰ small quantities of PH_3 :



Metal phosphites in H_2O are reduced in low yield¹¹ to PH_3 .

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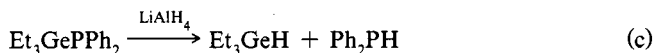
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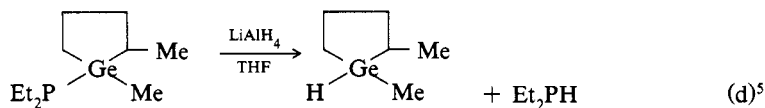
where $\text{R} = \text{Me}$, Et , CH_2Ph , $n\text{-Bu}$, C_6H_{11} , Ph . Yields range from 68 to 80%. Because $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ is readily available, the reaction is good for preparing large quantities² (50–400 mmol) of Me_2PH . Tetraphenyldiphosphine is reduced³ to Ph_2PH :



Germanium–P bond cleavage by LiAlH_4 yields⁴ Ph_2PH :



or⁵ Et_2PH :

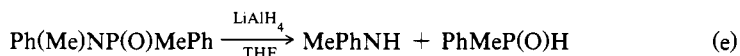


1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi

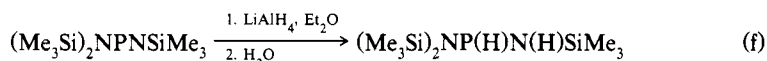
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Lithium tetrahydroborate can substitute for LiAlH_4 . The LiBH_4 reduction occurs with inversion of configuration at Ge, whereas LiAlH_4 cleavage occurs with retention of configuration.

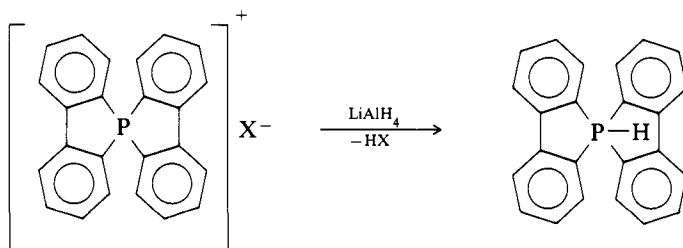
Lithium tetrahydroaluminate cleavage of Ph(Me)NP(O)MePh occurs⁶ at 25°C in THF:



In contrast, LiAlH_4 reduction of $(\text{Me}_3\text{Si})_2\text{NPNSiMe}_3$ followed by reaction workup in the presence of H_2O (or D_2O) yields a bis(amino)phosphine product⁷.



Lithium tetrahydroaluminate or LiBH_4 react with the spirophosphonium salt to form the corresponding P-H -phosphorane⁸:



Reduction of phosphonium salts as a route to tertiary phosphines is common, but its use for the synthesis of P-H compounds is unusual.

(A.D. NORMAN)

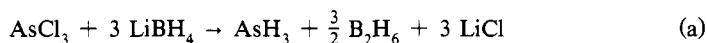
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1.5.5.3. with Compounds of Arsenic

1.5.5.3.1. Involving Halides.

Complex-hydride reductions of chloroarsines can be used to prepare AsH_3 and primary (RAsH_2) and secondary organoarsines (R_2AsH). These syntheses are efficient and convenient for laboratory quantities of arsines¹⁻³.

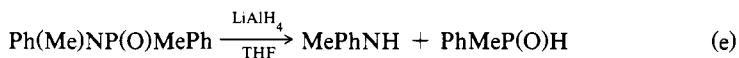
Arsenic(III) trichloride reacts^{1,2} with LiAlH_4 or LiBH_4 in ethers at -80°C :



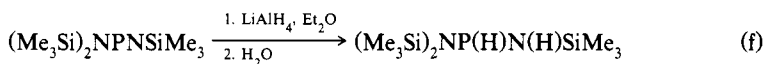
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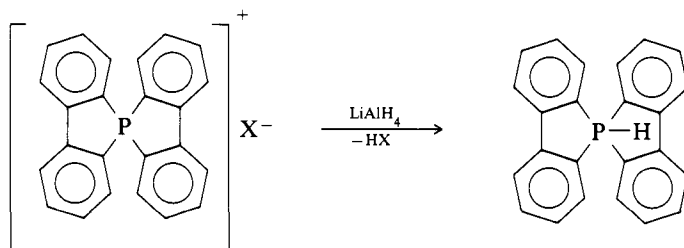
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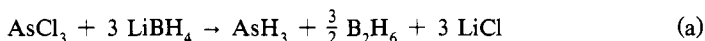
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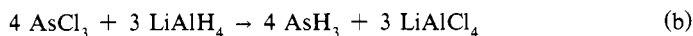
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Arsenic(III) trichloride reacts^{1,2} with LiAlH_4 or LiBH_4 in ethers at -80°C :



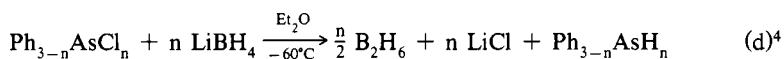


Because only 1 equiv of hydride from LiBH_4 reacts, the reaction is inefficient, although AsH_3 yields of 93% based on Eq. (a) occur. At higher T, yields are lower. At RT, AsCl_3 is reduced to elemental As. Reduction by LiAlH_4 proceeds more rapidly. At -78°C , yields of 10–15% are obtained.

Reduction by LiAlH_4 of RAsCl_2 or R_2AsCl (R = alkyl, aryl) occurs in ethers:



yields^{2,3} (%) are: CF_3AsH_2 , 49; PhAsH_2 , 54; Me_2AsH , 68; Et_2AsH , 80; $n\text{-Pr}_2\text{AsH}$, 57; $n\text{-Bu}_2\text{AsH}$, 73; $(\text{C}_6\text{H}_{11})_2\text{AsH}$, 77; Ph_2AsH and $(\text{CF}_3)_2\text{AsH}$, 16. Phenylarsines ($n = 1, 2$) also form in low-T LiBH_4 reductions of the respective chloroarsines:

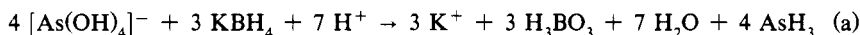


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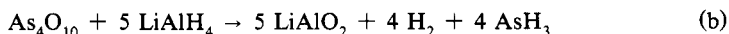
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Alkali-metal tetrahydroborates reduce oxyarsenic(III) species in H_2O to AsH_3 in high yields^{1,2}. Potassium tetrahydroborate in base, when added dropwise to aq acid (H_2SO_4), reacts as:



Arsine yields of 59%, along with traces of As_2H arising from As_2H_4 decomposition, are claimed³.

Solid As_4O_{10} reacts with LiAlH_4 at $148\text{--}170^\circ\text{C}$, yielding⁴ AsH_3 :

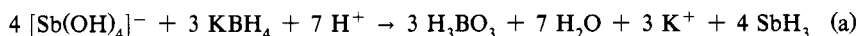


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1.5.5.4. with Compounds of Antimony.

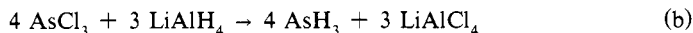
Reactions of complex hydrides with Sb compounds are effective for stibine syntheses¹. Metal tetrahydroborate reductions of Sb compounds in both H_2O and nonaqueous media occur². Dropwise addition of a basic $[\text{Sb}(\text{OH})_4]^-$ - KBH_4 soln to aqueous acid forms SbH_3 in 95% yield³:



Product yield is optimized by slow reagent addition. Antimony trichloride in saturated

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 51

1.5.5. by Reaction of Complex Hydrides

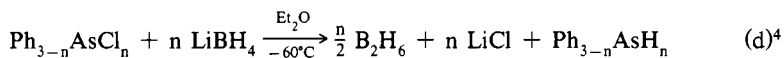


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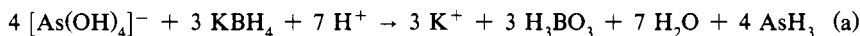


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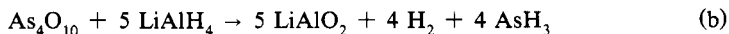
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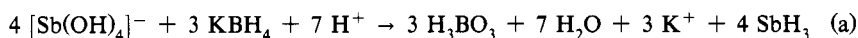


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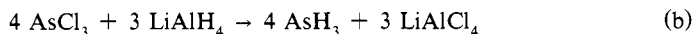
Reactions of complex hydrides with Sb compounds are effective for stibine syntheses¹. Metal tetrahydroborate reductions of Sb compounds in both H_2O and nonaqueous media occur². Dropwise addition of a basic $[\text{Sb}(\text{OH})_4]^- \text{--} \text{KBH}_4$ soln to aqueous acid forms SbH_3 in 95% yield³:



Product yield is optimized by slow reagent addition. Antimony trichloride in saturated

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 51

1.5.5. by Reaction of Complex Hydrides

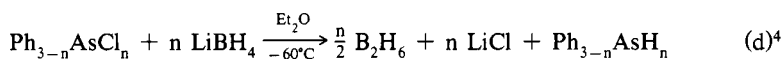


Because only 1 equiv of hydride from LiBH_4 reacts, the reaction is inefficient, although AsH_3 yields of 93% based on Eq. (a) occur. At higher T, yields are lower. At RT, AsCl_3 is reduced to elemental As. Reduction by LiAlH_4 proceeds more rapidly. At -78°C , yields of 10–15% are obtained.

Reduction by LiAlH_4 of RAsCl_2 or R_2AsCl (R = alkyl, aryl) occurs in ethers:



yields^{2,3} (%) are: CF_3AsH_2 , 49; PhAsH_2 , 54; Me_2AsH , 68; Et_2AsH , 80; $n\text{-Pr}_2\text{AsH}$, 57; $n\text{-Bu}_2\text{AsH}$, 73; $(\text{C}_6\text{H}_{11})_2\text{AsH}$, 77; Ph_2AsH and $(\text{CF}_3)_2\text{AsH}$, 16. Phenylarsines ($n = 1, 2$) also form in low-T LiBH_4 reductions of the respective chloroarsines:

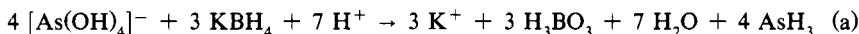


(A.D. NORMAN)

1. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
2. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
3. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
4. E. Wiberg, K. Mödritzer, *Z. Naturforsch., Teil B*, **12**, 127 (1957).

1.5.5.3.2. Involving Oxygen Compounds.

Alkali-metal tetrahydroborates reduce oxyarsenic(III) species in H_2O to AsH_3 in high yields^{1,2}. Potassium tetrahydroborate in base, when added dropwise to aq acid (H_2SO_4), reacts as:



Arsine yields of 59%, along with traces of As_2H arising from As_2H_4 decomposition, are claimed³.

Solid As_4O_{10} reacts with LiAlH_4 at $148\text{--}170^\circ\text{C}$, yielding⁴ AsH_3 :

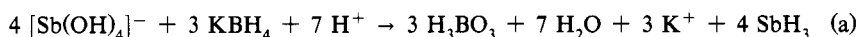


(A.D. NORMAN)

1. B. D. James, M. G. H. Walbridge, *Prog. Inorg. Chem.*, **11**, 99 (1970).
2. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
3. W. L. Jolly, J. E. Drake, *Inorg. Synth.*, **7**, 34 (1966).
4. J. M. Bellama, A. G. MacDiarmid, *Inorg. Chem.*, **7**, 2070 (1968).

1.5.5.4. with Compounds of Antimony.

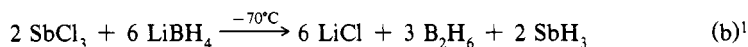
Reactions of complex hydrides with Sb compounds are effective for stibine syntheses¹. Metal tetrahydroborate reductions of Sb compounds in both H_2O and nonaqueous media occur². Dropwise addition of a basic $[\text{Sb}(\text{OH})_4]^-$ – KBH_4 soln to aqueous acid forms SbH_3 in 95% yield³:



Product yield is optimized by slow reagent addition. Antimony trichloride in saturated

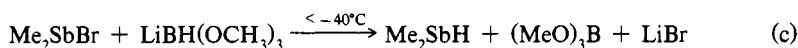
aq NaCl is reduced to SbH_3 by aq NaBH_4 soln⁴. Yields of SbH_3 up to 70% using a $\text{NaBH}_4:\text{Na}_3\text{SbCl}_6$ ratio greater than 10 are claimed.

Alkali-metal tetrahydroborates in ethers reduce SbCl_3 :

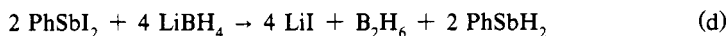


The synthesis of SbH_3 from MBH_4 ($\text{M} = \text{Li, Na, K}$) reduction of SbCl_5 in diglyme at 25°C is claimed⁵.

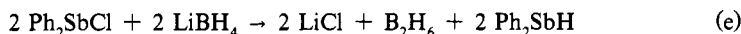
Methylstibine and Me_2SbH form from reaction of Me_2SbBr with NaBH_4 in diglyme. From the cleaner reduction using $\text{LiBH}(\text{OCH}_3)_3$:



Me_2SbH yields of 35% are obtained⁶. Lithium tetrahydroborate reduction of PhSbI_2 :



and Ph_2SbCl in ether below -50°C produces PhSbH_2 and Ph_2SbH , respectively^{7,8}:

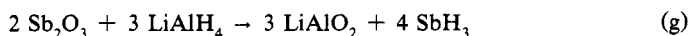


Lower yields (<40%) occur when LiBH_4 is replaced with LiAlH_4 . Similarly, $[\text{PhSbCl}_5]\text{NH}_4$ reacts with LiBH_4 or LiAlH_4 to form PhSbH_2 , with no evidence¹ of PhSbH_4 .

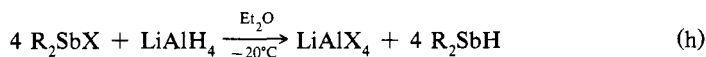
Lithium tetrahydroaluminate reduces² SbCl_3 in ether to SbH_3 :



An analogous $\text{LiAlH}_4\text{-SbCl}_5$ reaction yields² SbH_3 , but no SbH_5 . Reaction of solid powdered Sb_2O_3 with a deficit of LiAlH_4 at $148\text{--}170^\circ\text{C}$ yields⁹ SbH_3 .



High yields of dialkyl- and monoalkylstibines result from the respective halo-stibines with LiAlH_4 in ethers ($n\text{-Bu}_2\text{O}$ or Et_2O)^{1,10,11} below -20°C :



where $\text{X} = \text{Cl, Br}$; $\text{R} = \text{Me, Et, t-Bu, C}_6\text{H}_{11}$;



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

(A.D. NORMAN)

1. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
2. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
3. W. L. Jolly, J. E. Drake, *Inorg. Synth.*, **7**, 34 (1963). A preferred synthesis for AsH_3 .
4. A. D. Zorm, I. A. Frolov, U. S. Zaburdaev, S. A. Nosyrev, *J. Appl. Chem. USSR (Engl. Transl.)*, **47**, 1193 (1974); *Chem. Abstr.*, **81**, 173,481 (1974).
5. R. G. Gordon, Belg. Pat. 890,356 (1982); *Chem. Abstr.*, **96**, 199,887 (1982).
6. A. B. Burg, L. R. Grant, *J. Am. Chem. Soc.*, **81**, 1 (1959).
7. E. Wiberg, K. Mödritzer, *Z. Naturforsch., Teil B*, **12**, 128 (1957).

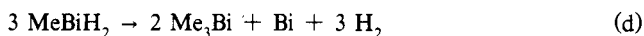
8. E. Wiberg, K. Mödritzer, *Z. Naturforsch., Teil B*, 12, 131 (1957).
9. J. M. Bellama, A. G. MacDiarmid, *Inorg. Chem.*, 7, 2070 (1968).
10. K. Issleib, B. Hamann, *Z. Anorg. Allg. Chem.*, 339, 289 (1965).
11. A. L. Reingold, P. Choudhury, M. F. El-Shazly, *Synth. React. Inorg. Metal-Org. Chem.*, 8, 453 (1978).

1.5.5.5. with Compounds of Bismuth.

Bismuthine, MeBiH_2 and Me_2BiH can be prepared by LiAlH_4 reduction of halobismuthines^{1,2}. Yields are low, even at -110°C :



The alkylbismuthines are thermally unstable³; e.g., MeBiH_2 disproportionates above -45°C :



Compounds containing Bi—H bonds are not isolated⁴ from reactions of LiAlH_4 with PhBiBr_2 , Ph_2BiCl or Ph_3BiCl_2 .

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1. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
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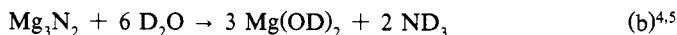
1.5.6. by Industrial Processes

1.5.6.1. Involving Compounds of Nitrogen.

Ammonia is obtained industrially from reaction of N_2 and H_2 gas at high P (1×10^5 Pa) and T (500°C) over Fe or $\text{Fe/Fe}_2\text{O}_3$ catalysts¹⁻³:



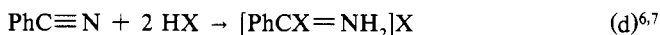
Ammonia- D_3 can be prepared by replacement of H_2 by D_2 ; however, it is better prepared by the deuterolysis of a metal nitride:



Ammonium salts form by direct reaction of amines with mineral acids, e.g.:



Reactions of nitriles or isocyanates with protonic acids yield imines:



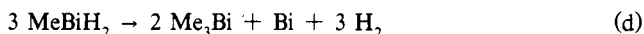
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Compounds containing $\text{Bi}-\text{H}$ bonds are not isolated⁴ from reactions of LiAlH_4 with PhBiBr_2 , Ph_2BiCl or Ph_3BiCl_2 .

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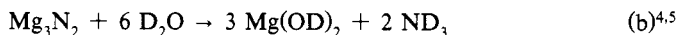
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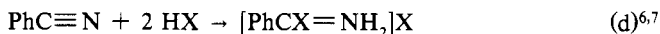
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Ammonium salts form by direct reaction of amines with mineral acids, e.g.:



Reactions of nitriles or isocyanates with protonic acids yield imines:



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 53

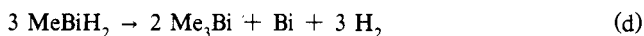
8. E. Wiberg, K. Mödritzer, *Z. Naturforsch., Teil B*, 12, 131 (1957).
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(A.D. NORMAN)

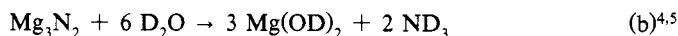
1. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.
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3. L. D. Freedman, *Chem. Rev.*, 82, 15 (1982).
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1.5.6. by Industrial Processes**1.5.6.1. Involving Compounds of Nitrogen.**

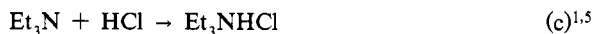
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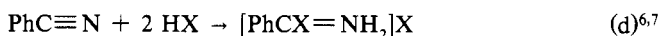
Ammonia- D_3 can be prepared by replacement of H_2 by D_2 ; however, it is better prepared by the deuteroysis of a metal nitride:



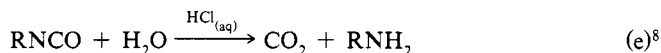
Ammonium salts form by direct reaction of amines with mineral acids, e.g.:



Reactions of nitriles or isocyanates with protonic acids yield imines:



where X = Cl, Br; amines:



where R = alkyl, aryl; or amides:



Reduction of nitro compounds with metals (Fe, Sn, Zn, Mg) in aq acid is the major industrial synthetic route to primary amines:



where R = Et, n-Bu, Ph, etc. Similarly, reduction by carbon in hot steam forms PhNH_2 from PhNO_2 in high yields:



Reductions using H_2 directly, in the presence of homogenous¹¹ [e.g., $\text{Fe}(\text{CO})_5$] or heterogeneous (e.g., Pt)^{10,12} catalysts, also yield amines:



Hydrogen reduction of nitriles:



where R = alkyl, aryl; or imines:



where R and R' = alkyl, aryl, in the presence of catalysts is used to produce amines. Similar reduction of pyridine or its derivatives yields piperidines:



Nitrogen compounds containing N—H bonds for specialty chemical, drug or pharmaceutical applications are synthesized using the reactions (especially hydride reductions) discussed in §1.5.4.1 and 1.5.5.1. These small-scale syntheses are highly specialized and usually relatively expensive. Further information can be found in treatises on synthetic organic chemistry.

(A.D. NORMAN)

1. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
2. A. Ozaki, *Acc. Chem. Res.*, **14**, 16 (1981).
3. L. Axelrod, *Catal. Rev. Sci. Eng.*, **23**, 53 (1981).
4. L. K. Krannich, U. Thewalt, W. J. Cook, S. R. Jain, H. H. Sisler, *Inorg. Chem.*, **12**, 2304 (1973).
5. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
6. G. Tennant, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 385.

7. R. G. Coombes, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 305.
8. R. J. Lindsay, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979.
9. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961.
10. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 4th ed., Allyn and Bacon, Boston, 1983.
11. H. Alper, J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970).
12. J. R. Malpass, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 3.

1.5.6.2. Involving Compounds of Phosphorus.

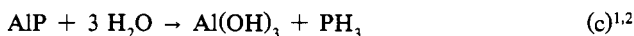
Phosphine is obtained by the alkaline hydrolysis of P_4 :



or the reduction of P_4 by the active metals (e.g., Zn, Mg) in H_2O :

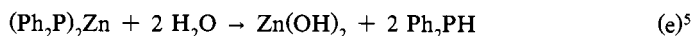
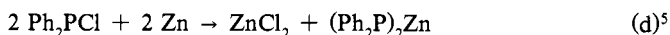


Large quantities of PH_3 can be obtained from metal-phosphide hydrolyses:

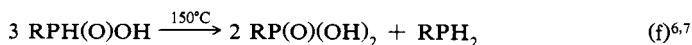


This method is adapted to large-scale PD_3 synthesis by substitution⁴ of D_2O for H_2O .

Primary and secondary phosphines, e.g., $PhPH_2$ and Ph_2PH , are prepared stepwise from the substituted phosphinous chlorides by metal reduction and hydrolysis:



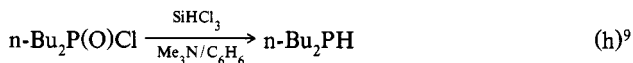
Disproportionation of alkylphosphinic acid or alkylphosphinates yields primary phosphines.



where $R = Me, Et, Ph$, etc. Reaction of P_4 with $MeNH_2$ at $350^\circ C$, over active carbon yields methylphosphines:



Specialty-chemical level production (kilograms) of phosphines is achieved by hydride reductions of halophosphines, phosphonyl halides and esters and phosphinyl halides and esters, e.g.:



Phosphorus acids or their salts containing $P-H$ bonds are obtained commercially from hydrolysis of elemental phosphorus or phosphorus halides, under controlled conditions. Variations result in different product mixtures. Phosphorous acid forms in reactions^{1,6,11} of PCl_3 with H_2O at $185-195^\circ C$:

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 55

1.5.6. by Industrial Processes

7. R. G. Coombes, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 305.
8. R. J. Lindsay, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979.
9. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961.
10. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 4th ed., Allyn and Bacon, Boston, 1983.
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1.5.6.2. Involving Compounds of Phosphorus.

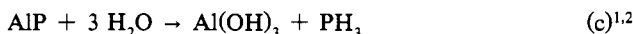
Phosphine is obtained by the alkaline hydrolysis of P_4 :



or the reduction of P_4 by the active metals (e.g., Zn, Mg) in H_2O :

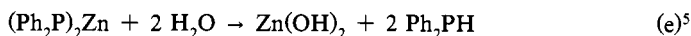
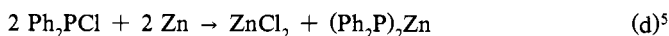


Large quantities of PH_3 can be obtained from metal-phosphide hydrolyses:

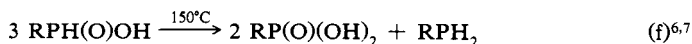


This method is adapted to large-scale PD_3 synthesis by substitution⁴ of D_2O for H_2O .

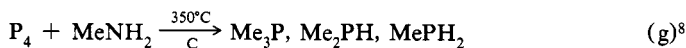
Primary and secondary phosphines, e.g., $PhPH_2$ and Ph_2PH , are prepared stepwise from the substituted phosphinous chlorides by metal reduction and hydrolysis:



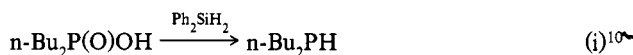
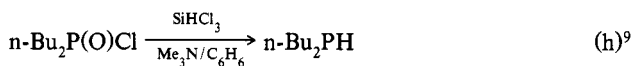
Disproportionation of alkylphosphinic acid or alkylphosphinates yields primary phosphines.



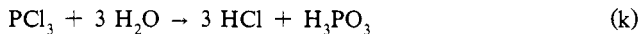
where R = Me, Et, Ph, etc. Reaction of P_4 with $MeNH_2$ at $350^\circ C$, over active carbon yields methylphosphines:



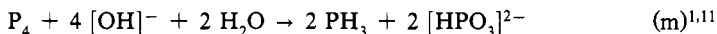
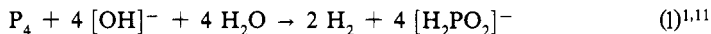
Specialty-chemical level production (kilograms) of phosphines is achieved by hydride reductions of halophosphines, phosphonyl halides and esters and phosphinyl halides and esters, e.g.:



Phosphorus acids or their salts containing P—H bonds are obtained commercially from hydrolysis of elemental phosphorus or phosphorus halides, under controlled conditions. Variations result in different product mixtures. Phosphorous acid forms in reactions^{1,6,11} of PCl_3 with H_2O at $185-195^\circ C$:



At lower T (e.g., 0°C) in carbonate-buffered H_2O , mixtures of acid salts, such as $[\text{H}_2\text{P}_2\text{O}_5]^{2-}$ and $[\text{HP}_2\text{O}_3]^{2-}$ in addition to $[\text{HPO}_3]^{2-}$, $[\text{P}_2\text{O}_6]^{4-}$, $[\text{PO}_4]^{3-}$ and $[\text{P}_2\text{O}_7]^{4-}$, are formed¹¹. Reaction of P_4 with basic H_2O at 80–90°C yields hypophosphites:

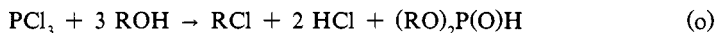


Salts of hypodiphosphorous acid form in reactions^{6,11} of red phosphorus with aq NaClO_2 :

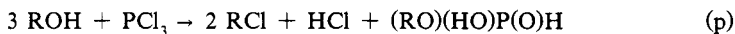


and in lesser amounts in complex mixtures from the reaction of P_2I_4 with aq base¹² H_2O .

Alcohols react with PCl_3 to form o-dialkylphosphonates:



where R = alkyl, or o-monoalkylphosphonates:

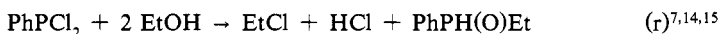


depending on reaction conditions^{11,13}. At high T or upon thermolysis of $(\text{RO})_2\text{P}(\text{O})\text{H}$, o-monoalkylphosphonates form^{11,13}.

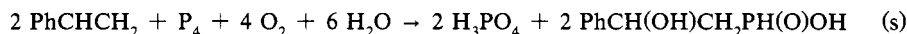
Alkyl- or arylphosphinic acids form from reaction of H_2O with dialkylphosphinous halides at 100°C^{1,7}:



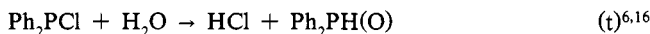
where R = Me, Et, i-Pr, t-C₄H₉, CF₃, PhCH₂, Ph, etc. Alcoholysis of RPhCl_2 yields o-alkylphosphinates:



Reaction of olefins with P_4 , O_2 and H_2O yields β -hydroxyphosphinic acids in a complex reaction⁷:



Hydrolysis of phosphinous chlorides yields the corresponding phosphine oxides, as:



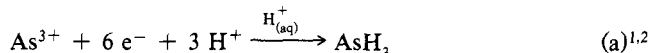
(A.D. NORMAN)

1. A. F. Toy, in *Comprehensive Inorganic Chemistry*, A. F. Trotman-Dickenson, ed., Vol. 2, Pergamon Press, Oxford, 1973, p. 389.
2. E. Fluck, *Top. Curr. Chem.*, **35**, 1 (1973).
3. M. G. Palmer, Br. Pat. 943,281 (1963); *Chem. Abstr.*, **60**, 6524 (1964).
4. R. C. Marriott, J. D. Odom, C. T. Sears Jr., *Inorg. Synth.*, **14**, 1 (1973).
5. L. Maier, *Prog. Inorg. Chem.*, **5**, 27 (1963).
6. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, London, 1976.
7. A. W. Frank, *Chem. Rev.*, **61**, 389 (1961).
8. K. Hestermann, J. Joedden, G. Heymer, Ger. Pat. 2,721,425 (1979); *Chem. Abstr.*, **90**, 152,353 (1979).

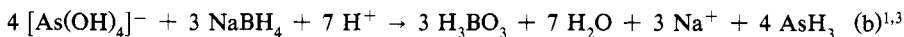
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1.5.6.3. Involving Compounds of Arsenic.

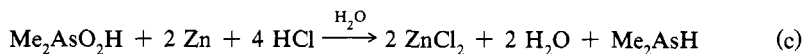
Arsine is prepared electrochemically by reduction of As(III) species:



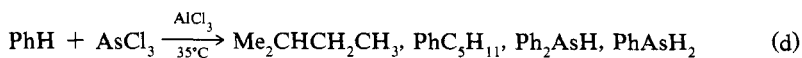
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Limited commercial use is made of the Zn reduction of $\text{Me}_2\text{AsO}(\text{OH})$ to form⁴ Me_2AsH :



In the presence of AlCl_3 , benzene reacts with AsCl_3 , forming a mixture of products⁵ that includes PhAsH_2 and Ph_2AsH :

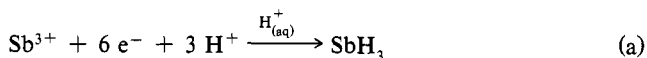


(A.D. NORMAN)

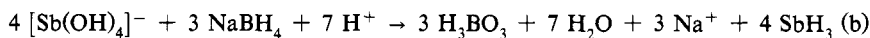
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1.5.6.4. Involving Compounds of Antimony.

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(A.D. NORMAN)

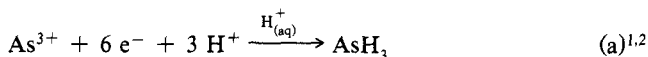
1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 57

1.5.6. by Industrial Processes

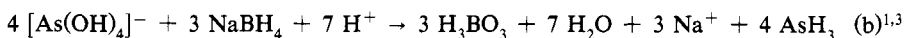
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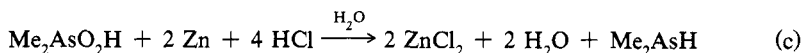
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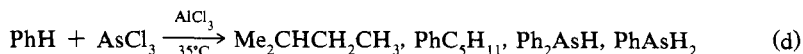
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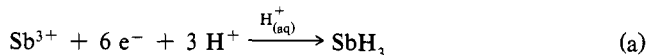


(A.D. NORMAN)

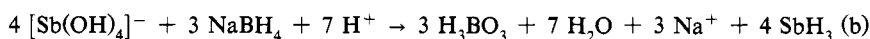
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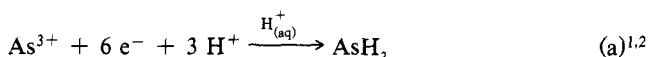
(A.D. NORMAN)

1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 57
 1.5.6. by Industrial Processes

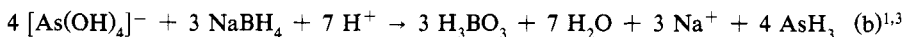
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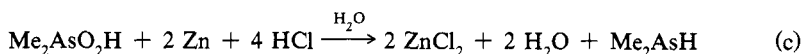
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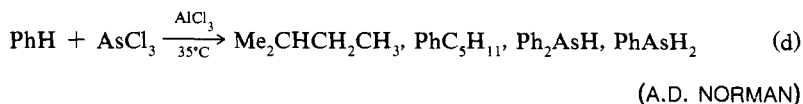
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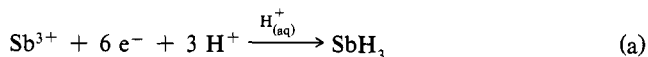
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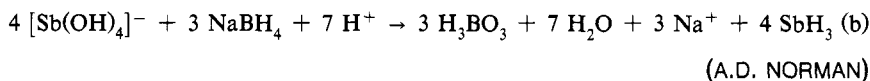
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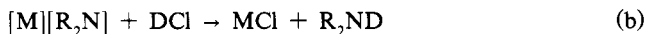
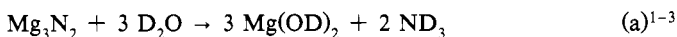
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1.5.7. The Synthesis of Deuterium Derivatives

1.5.7.1. by Interconversion of Deuterated Compounds

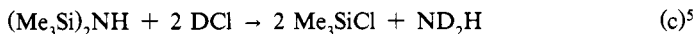
1.5.7.1.1. Involving Nitrogen.

Protonic (deuterio) acid solvolysis of -ide salts is a route to compounds with N-D bonds. Alkali or alkaline-earth nitrides or amides react with D₂O or DCl to form products in high isotopic purity, e.g.:

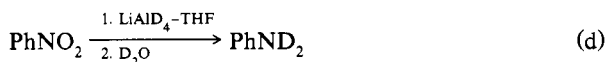


where R = alkyl, aryl; M = Li, Na, K. Such reactions with DCl can proceed to deuterio ammonium [NH₄]⁺ ions if xs DCl is present.

Cleavages of metal- or nonmetal-N bonds by D₂O or ROD yield N-D bonds, although these are seldom synthetically important⁴. Reactions of primary or secondary amines can produce mixed hydro-deuterio products:



Complex metal hydroborate-d₄ and hydroaluminate-d₄ reductions are used in syntheses of deuterioamines. Reactions of nitro compounds:



and imines:



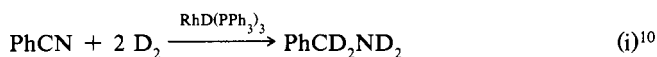
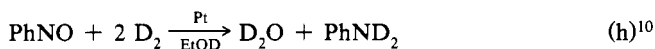
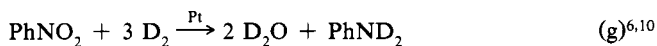
with LiAlD₄ illustrate these. For details, treatises on organic chemistry should be consulted⁶⁻⁸.

Reaction⁹ of N₂ with D₂ gas at high T and P yields ND₃:



however, the process is useful mainly only for large quantities of ND₃ because the apparatus required is complex.

Catalytic deuterium reduction of nitrogen compounds occurs readily, e.g.:



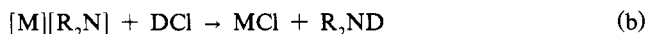
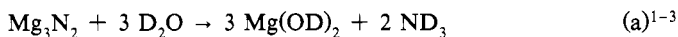
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1.5.7.1. by Interconversion of Deuterated Compounds

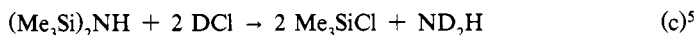
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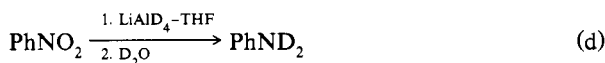


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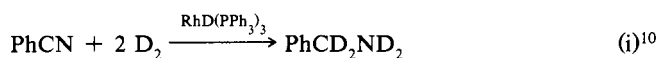
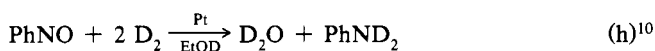
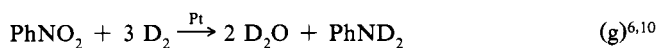
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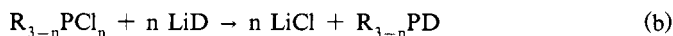
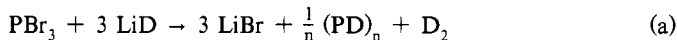
Details can be found in organic synthesis texts^{6,10}.

(A.D. NORMAN)

1. G. Brauer, M. Baudler, *Handbook of Preparative Inorganic Chemistry*, G. Brauer, ed., 2nd ed., Vol. 1, Academic Press, New York, 1963.
2. L. K. Krannich, U. Thewalt, W. J. Cook, S. R. Jain, H. H. Sisler, *Inorg. Chem.*, **12**, 2304 (1973).
3. H. L. Crespi, J. J. Katz, in *Inorganic Isotopic Synthesis*, R. H. Herber, ed., Benjamin, New York, 1962, p. 14.
4. D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).
5. D. A. Armitage, *Organomet. Chem.*, **10**, 86 (1980).
6. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
7. H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972.
8. J. R. Malpass, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 3.
9. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
10. C. A. Beuhler, D. E. Pearson, in *Survey of Organic Synthesis*, Vol. 2, Wiley-Interscience, New York, 1977, p. 391.

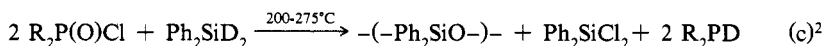
1.5.7.1.2. Involving Phosphorus.

Ionic hydride reductions of halophosphorus compounds that are effective for phosphine syntheses are adaptable to deuteriophosphine syntheses. Lithium-deuteride reductions yield phosphorus subhydride, phosphine or alkyl- or arylphosphines^{1,2}:

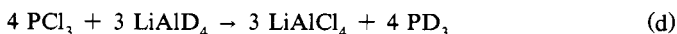


where R = alkyl, aryl; n = 1–3. However, covalent or complex hydride reductants are preferred.

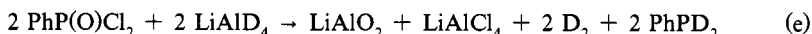
Covalent deuterio-hydrides, e.g., silanes or stannanes, are used in deuteriophosphine synthesis³, e.g.:



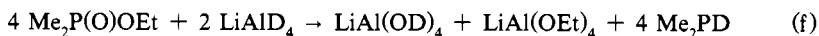
Complex hydride reductions are adapted to deuteriophosphine syntheses^{2,3}. The isotopic purity of the products is high. Reactions of LiAlD_4 with chlorophosphines:



phosphonyl chlorides:

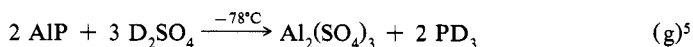


and phosphinate esters:



illustrate these.

Solvolysis of -ide salts with D_2O yields deuteriophosphines. Reaction of D_2SO_4 or D_2O with AlP^4 or Ca_3P_2^5 produces PD_3 :



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 59
 1.5.7. The Synthesis of Deuterium Derivatives
 1.5.7.1. by Interconversion of Deuterated Compounds

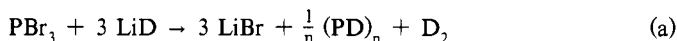
Details can be found in organic synthesis texts^{6,10}.

(A.D. NORMAN)

1. G. Brauer, M. Baudler, *Handbook of Preparative Inorganic Chemistry*, G. Brauer, ed., 2nd ed., Vol. 1, Academic Press, New York, 1963.
2. L. K. Krannich, U. Thewalt, W. J. Cook, S. R. Jain, H. H. Sisler, *Inorg. Chem.*, **12**, 2304 (1973).
3. H. L. Crespi, J. J. Katz, in *Inorganic Isotopic Synthesis*, R. H. Herber, ed., Benjamin, New York, 1962, p. 14.
4. D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).
5. D. A. Armitage, *Organomet. Chem.*, **10**, 86 (1980).
6. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
7. H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972.
8. J. R. Malpass, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 2, I. O. Sutherland, ed., Pergamon Press, New York, 1979, p. 3.
9. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
10. C. A. Beuhler, D. E. Pearson, in *Survey of Organic Synthesis*, Vol. 2, Wiley-Interscience, New York, 1977, p. 391.

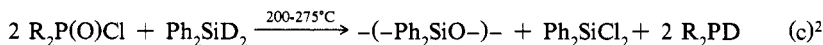
1.5.7.1.2. Involving Phosphorus.

Ionic hydride reductions of halophosphorus compounds that are effective for phosphine syntheses are adaptable to deuteriophosphine syntheses. Lithium-deuteride reductions yield phosphorus subhydride, phosphine or alkyl- or arylphosphines^{1,2}:

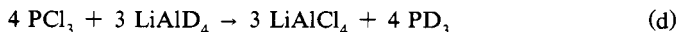


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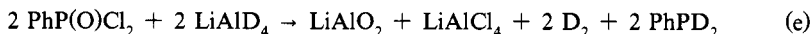
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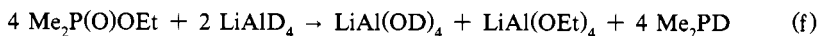
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phosphonyl chlorides:

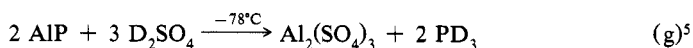


and phosphinate esters:

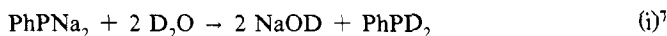
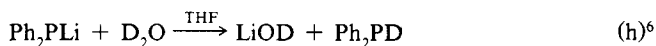


illustrate these.

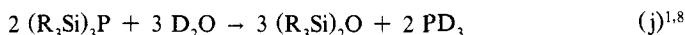
Solvolysis of -ide salts with D_2O yields deuteriophosphines. Reaction of D_2SO_4 or D_2O with AlP ⁴ or Ca_3P_2 ⁵ produces PD_3 :



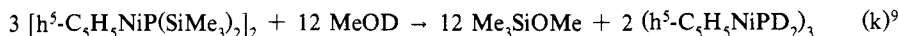
From the $\text{D}_2\text{O}-\text{Ca}_3\text{P}_2$ reaction, P_2D_4 is obtained also. When treated with D_2O alkali-metal organophosphides produce deuteriophosphines in high yields ($> 75\%$) and isotopically pure, e.g.:



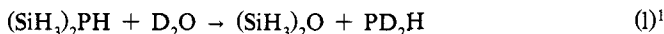
Cleavage of Si—P bonds by D_2O produces P—D bonds:



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



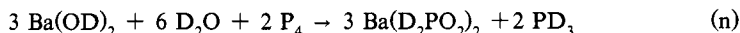
From primary or secondary silylphosphine deuterolysis, mixed hydro–deuterio products form:



Deuterolysis of PI_3 produces⁴ PD_3 , whereas D_2O and PCl_3 yield D_3PO_3 :



Reaction of basic D_2O with elemental phosphorus produces $\text{Ba}(\text{D}_2\text{PO}_2)_2$ and PD_3 in high yields⁴:



(A.D. NORMAN)

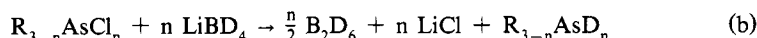
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2. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
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4. H. L. Crespi, J. J. Katz, in *Inorganic Isotopic Syntheses*, R. H. Herber, ed., Benjamin, New York, 1962, p. 14.
5. R. C. Marriott, J. D. Odom, C. T. Sears, Jr., *Inorg. Synth.*, **14**, 1 (1973).
6. V. D. Bianco, S. Doronzo, *Inorg. Synth.*, **16**, 161 (1976).
7. L. Horner, P. Beck, H. Hofman, *Chem. Ber.*, **92**, 2088 (1959).
8. H. Bürger, U. Goetze, *J. Organomet. Chem.*, **12**, 451 (1968).
9. H. Schäffer, *Z. Anorg. Allg. Chem.*, **459**, 157 (1979).

1.5.7.1.3. Involving Arsenic.

High yields of isotopically pure AsD_3 form upon dropwise addition¹ of D_2O to Na_3As :



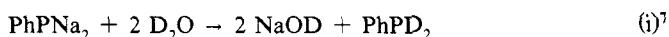
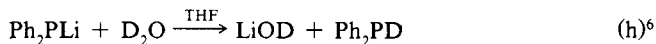
Lithium tetrahydroborate- d_4 reduction of chloroarsines yields deutoarsines, in reactions¹⁻³ more efficient than those using LiAlD_4 .



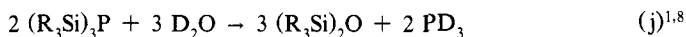
Deuterolysis of Si—As or Ge—As bonds produces As—D bonds:

60 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.7. The Synthesis of Deuterium Derivatives
 1.5.7.1. by Interconversion of Deuterated Compounds

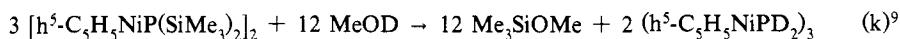
From the $\text{D}_2\text{O}-\text{Ca}_3\text{P}_2$ reaction, P_2D_4 is obtained also. When treated with D_2O alkali-metal organophosphides produce deuteriophosphines in high yields ($>75\%$) and isotopically pure, e.g.:



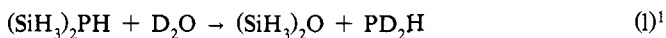
Cleavage of Si—P bonds by D_2O produces P—D bonds:



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



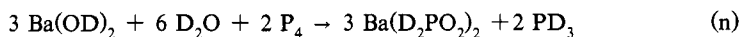
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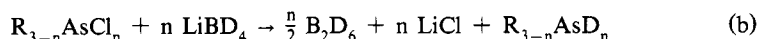
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1.5.7.1.3. Involving Arsenic.

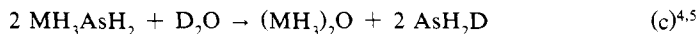
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Deuterolysis of Si—As or Ge—As bonds produces As—D bonds:



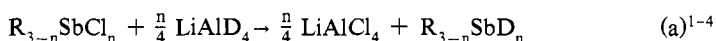
where M = Si, Ge.

(A.D. NORMAN)

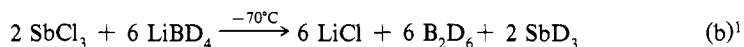
1. J. E. Drake, C. Riddle, *Inorg. Synth.*, 13, 14 (1972).
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High isotopic purity stibines form from LiAlD_4 with halostibines in ether, e.g.:



where $n = 1-3$; R = alkyl, aryl. Stibine- d_3 also forms in the LiBD_4 reduction of SbCl_3 at -70°C in ethers.

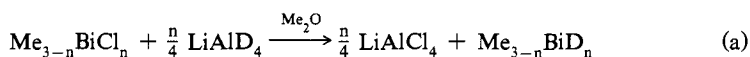


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Deuteriobismuthines form in the LiAlD_4 reduction of the corresponding chlorides; however, bismuthines¹ are thermally unstable above -45°C :



where $n = 1,2$.

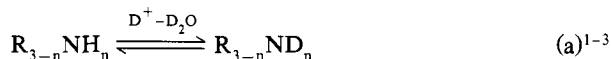
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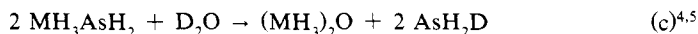
1.5.7.2. by Isotopic Enrichment Using Chemical Reactions

1.5.7.2.1. of Nitrogen Compounds.

Exchange of amine hydrogen atoms with deuterated hydroxylic solvents occurs rapidly, especially upon acid catalysis:



1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi 61
 1.5.7. The Synthesis of Deuterium Derivatives



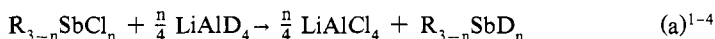
where M = Si, Ge.

(A.D. NORMAN)

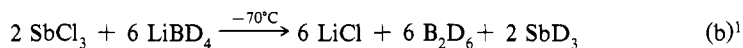
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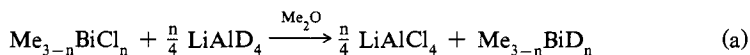


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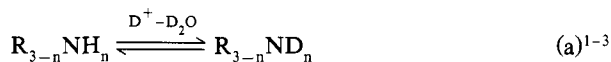
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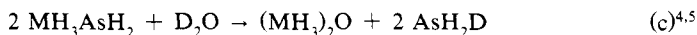
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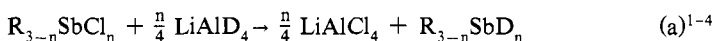
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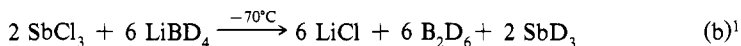
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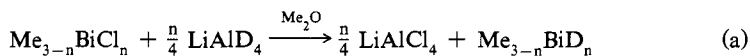


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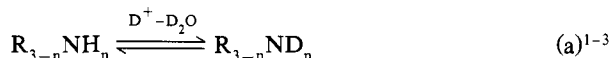
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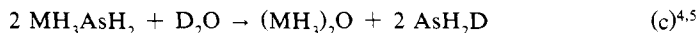
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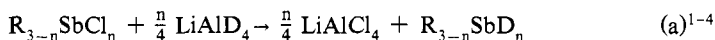
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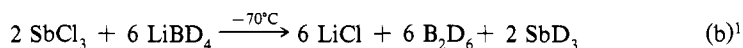
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4. A. L. Reingold, P. Choudhury, M. F. El-Shazly, *Synth. React. Inorg. Metal-Org. Chem.*, **8**, 453 (1978).

1.5.7.1.5. Involving Bismuth.

Deuteriobismuthines form in the LiAlD_4 reduction of the corresponding chlorides; however, bismuthines¹ are thermally unstable above -45°C :



where $n = 1, 2$.

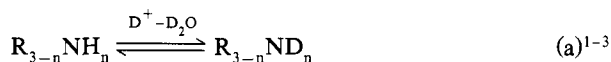
(A.D. NORMAN)

1. L. D. Freedman, G. O. Doak, *Chem. Rev.*, **82**, 15 (1982).

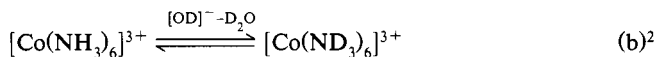
1.5.7.2. by Isotopic Enrichment Using Chemical Reactions

1.5.7.2.1. of Nitrogen Compounds.

Exchange of amine hydrogen atoms with deuterated hydroxylic solvents occurs rapidly, especially upon acid catalysis:



where R = alkyl, aryl; n = 1–3. Under similar conditions organic amides and metal amines undergo exchange with D₂O also.



(A.D. NORMAN)

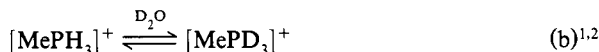
1. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
2. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
3. A. I. Shatenshtein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.

1.5.7.2.2. of Phosphorous Compounds.

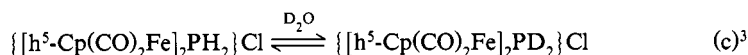
Hydrogen exchange between phosphines and deuterated hydroxylic solvents occurs slowly, the rate depending on the acidity of the phosphine. In the presence of acid or base catalysts, exchange is faster and the reactions can be used for deuteriophosphine synthesis¹, e.g.:



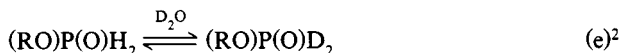
Phosphonium ions exchange with acidic deuterium sources to form P—D bond-containing products. Alkylphosphoniums react with D₂O as:



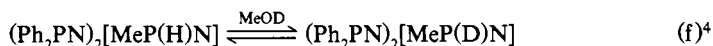
Acidic phosphido metal complexes exchange similarly, in instances where the complex is resistant to solvolysis:



Phosphinites and phosphinates exchange with deuterated media:



where R = alkyl, aryl. The P—H bonds in P—H phosphazenes exchange rapidly in MeOD to form deuterio products:

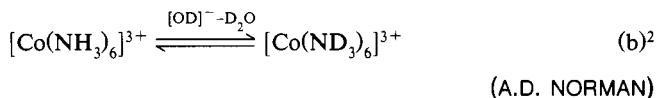


(A.D. NORMAN)

1. A. I. Shatenshtein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.
2. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
3. H. Schaeffer, *Angew. Chem., Int. Ed. Engl.*, 20, 608 (1981).
4. A. Schmidpeter, K. Blank, H. Eiletz, H. Smetana, C. Weinand, *Synth. React. Inorg. Metal-Organ. Chem.*, 7, 1 (1977).

62 1.5. Formation of Bonds between Hydrogen and N, P, As, Sb, Bi
 1.5.7. The Synthesis of Deuterium Derivatives
 1.5.7.2. by Isotopic Enrichment Using Chemical Reactions

where R = alkyl, aryl; n = 1–3. Under similar conditions organic amides and metal amines undergo exchange with D₂O also.



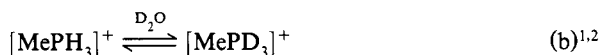
1. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
2. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
3. A. I. Shatenshtein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.

1.5.7.2.2. of Phosphorous Compounds.

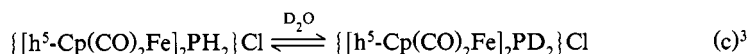
Hydrogen exchange between phosphines and deuterated hydroxylic solvents occurs slowly, the rate depending on the acidity of the phosphine. In the presence of acid or base catalysts, exchange is faster and the reactions can be used for deuteriophosphine synthesis¹, e.g.:



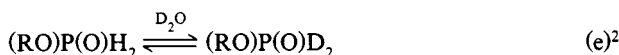
Phosphonium ions exchange with acidic deuterium sources to form P—D bond-containing products. Alkylphosphoniums react with D₂O as:



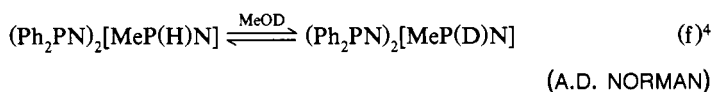
Acidic phosphido metal complexes exchange similarly, in instances where the complex is resistant to solvolysis:



Phosphinites and phosphinates exchange with deuterated media:



where R = alkyl, aryl. The P—H bonds in P—H phosphazenes exchange rapidly in MeOD to form deuterio products:

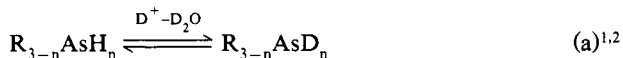


1. A. I. Shatenshtein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.
2. J. Emsley, D. Hall, *The Chemistry of Phosphorus*, Harper and Row, New York, 1976.
3. H. Schaeffer, *Angew. Chem., Int. Ed. Engl.*, 20, 608 (1981).
4. A. Schmidpeter, K. Blank, H. Eiletz, H. Smetana, C. Weinand, *Synth. React. Inorg. Metal-Organ. Chem.*, 7, 1 (1977).

1.5. Formation of Bonds Between Hydrogen and N, P, As, Sb, Bi	63
1.5.7. The Synthesis of Deuterium Derivatives	
1.5.7.2. by Isotopic Enrichment Using Chemical Reactions	

1.5.7.2.3. of Arsenic Compounds.

Hydrogen exchange between AsH_3 and D_2O occurs, at rates enhanced by either acid or base catalysts:



where R = alkyl, aryl; n = 1–3.

(A.D. NORMAN)

1. A. I. Shatenshtein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.
2. G. O. Doak, L. D. Freedman, *Organometallic Compounds of Arsenic, Antimony, and Bismuth*, Wiley-Interscience, New York, 1970.

1.6. Formation of Bonds between Hydrogen and Elements of Group IVB (C, Si, Ge, Sn, Pb)

1.6.1. Introduction

This chapter presents reactions by which bonds between hydrogen and C, Si, Ge, Sn or Pb are formed. The chemistry encompassed is large, because C—H bond formation is important in organic, organometallic, inorganic and biochemistry. Bond formations of interest in inorganic and organometallic chemistry receive greatest attention. Reactions in the realm of classical organic or biochemistry are treated more briefly.

Reactions are classed according to reagent or reaction type. Arbitrary characterization of systems must be made to allow their classification; thus X—H reagents are classed as protonic reagents if they participate in reactions as protonic acids, as is the case for molecules in which the electronegativity of X is appreciably greater than that of H. Otherwise, they are classed as simple hydrides if they contain hydrogen and one main element (binary) or hydrogen and two main elements (ternary, e.g., SiH_3PH_2) and complex hydrides if they contain hydride (H^-) moieties coordinated to a central element to form a complex anionic species, e.g., LiBH_4 .

(A.D. NORMAN)

1.6.2. from the Elements

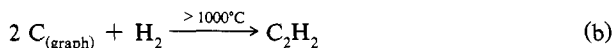
1.6.2.1. Giving Hydrides of Carbon

1.6.2.1.1. from Elemental Carbon.

Carbon does not react with H_2 at an appreciable rate under ordinary conditions¹. At high T and in the presence of catalysts reaction occurs as:



where $\Delta G^\circ(25^\circ\text{C}) = -50.7 \text{ kJ mol}^{-1}$. Powdered $\text{C}_{(\text{graph})}$ impregnated² with Ni, or C in the presence¹ of powdered Ni or Fe—Cr sponge³, reacts at 500–1000°C to form CH_4 along with small quantities of other hydrocarbons, e.g., C_2H_2 . At higher T, C_2H_2 becomes the dominant product:



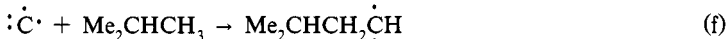
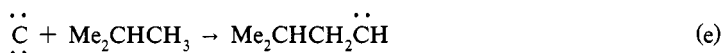
Atomic hydrogen, produced from H_2 in an electrical or microwave discharge, reacts with a carbon surface to form mainly C_2H_2 and CH_4 [e.g., Eq. (c)] along with small quantities of higher mol wt materials^{1,4}:



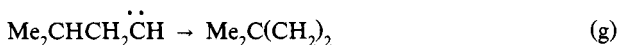
Reaction of H with ICN yields⁵ HCN:



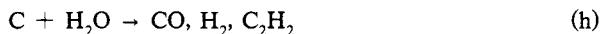
Carbon atoms, produced by thermal vaporization or laser irradiation of $\text{C}_{(\text{graph})}$ or in a carbon arc, react with H-containing substrates (e.g., alkanes, silanes, boranes, phosphines) to form C—H bonds^{1,6}. The carbon atoms, mixtures of (³P), (¹D) and (¹S) electronic-state species, react in the gas or condensed phase in a low-T matrix. Condensation of carbon atoms onto a cooled surface (-196°C) along with substrate results in reactions of C(¹S) atoms, before decay to the less reactive C(³P) species occurs. Condensation of C-arc produced carbon atoms with an alkane (e.g., iso- C_4H_{10}) at -196°C results in reaction of both singlet (¹S) and triplet (³P) species to form singlet and triplet carbenes:



Subsequent abstraction of hydrogen atoms from the substrate by the triplet carbene or insertion into a C—H bond by the singlet species can occur:



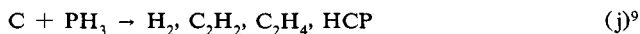
Laser-evaporated carbon atoms react⁷ with H_2O :



or⁸ B_5H_9 :



at low T to form primarily C_2H_2 and $\text{B}_5\text{C}_2\text{H}_7$, respectively. Phosphine passing through a carbon arc yields HCP:



Thermal C(³P) and hydrogen atoms in the gas phase, from C_3O_2 and H_2 in a microwave discharge, yield CH which subsequently reacts¹ to CH_4 and C_2H_2 . Carbon atoms from the $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$ reaction with NH_3 yield¹ CH_4 and CH_3NH_2 .

Small carbon molecules, C_2 , C_3 and C_4 , react with H-containing substrates, e.g.:

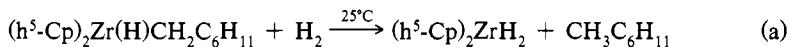


(A.D. NORMAN)

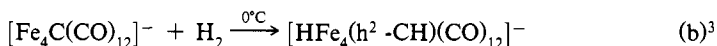
1. A. K. Holliday, G. Hughes, S. M. Walker, in *Comprehensive Inorganic Chemistry*, Vol. 6, A. F. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 1173.
2. S. D. Robertson, N. Mulder, R. Prins, *Carbon*, **13**, 348 (1975).
3. M. A. Qayzon, D. A. Reeve, *Carbon*, **14**, 199 (1976).
4. R. K. Gould, *J. Chem. Phys.*, **63**, 1825 (1975).
5. G. P. Horgan, M. R. Dunn, C. G. Freeman, M. J. McEwan, L. F. Phillips, *J. Phys. Chem.*, **76**, 1392 (1972).
6. P. S. Skell, J. S. Havel, M. J. McGlinchey, *Acc. Chem. Res.*, **6**, 97 (1973).
7. P. H. Kim, K. Taki, S. Namba, *Bull. Chem. Soc. Jpn.*, 2953 (1975).

8. S. R. Prince, R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 451 (1968).9. T. E. Gier, *J. Am. Chem. Soc.*, 83, 1769 (1961).**1.6.2.1.2. from Elemental Hydrogen.**

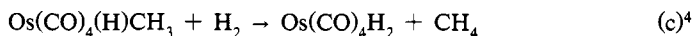
Main-group element or transition metal-carbon σ bonds can be cleaved by H_2 . Group IVA metal alkyls¹, e.g., Zr, react:



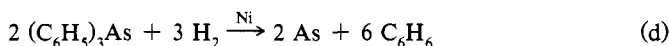
In the presence of Pd, H_2 reacts with $[PhCH_2Cr(H_2O)_5]^{2+}$ or $[CH_2=CHCH_2Co(CN)_5]^{3-}$ forming $PhCH_3$ and $CH_3CH=CH_2$, respectively.² The tetraironcarbonylcarbide cluster reacts with H_2 :



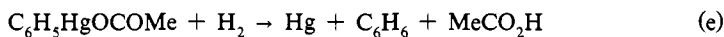
Cleavage of the hydrocarbon moieties from Pt or Os complexes occurs at 20°C, e.g.:



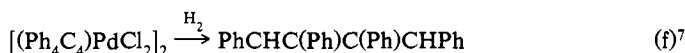
Triphenylarsine and Ph_3Bi with H_2 in the presence of Ni yield⁵ C_6H_6 , e.g.:



Phenylmercury(II) acetate with H_2 in the presence of Rh yields⁶ acetic acid and C_6H_6 :



Cleavage of π -bonded alkenes and alkynes from a metal complex can occur:

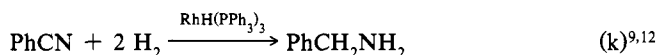
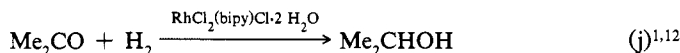
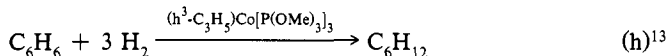


The formal cleavage of C—C bonds by H_2 in hydrogenolysis or cracking reactions, usually in the presence of metal catalysts⁸, e.g.:



is common (see treatises on organic chemistry)⁹.

Homogeneous or heterogeneous catalyzed H_2 reduction of unsaturated organic compounds arene, alkyne, alkene, ketone, oxime, nitrile and imine occurs readily^{1,4,6,8-12}, e.g.:



Hydrogenations using heterogeneous catalysts usually require above ambient T and H_2 pressures $\geq 10^3$ Pa. Homogeneous catalysts are often more selective and involve lower T (e.g., 25°C) and H_2 (ca. 10^2 Pa). Highly useful selectivity in hydrogenation is shown in reactions of H_2 with prochiral substrates in the presence of chiral catalysts, e.g., op-

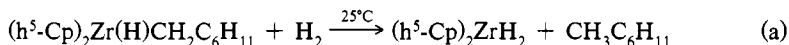
66 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.2. from the Elements
 1.6.2.1. Giving Hydrides of Carbon

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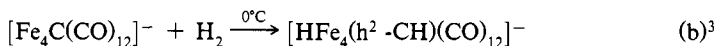
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1.6.2.1.2. from Elemental Hydrogen.

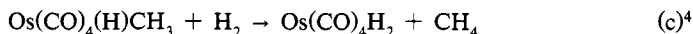
Main-group element or transition metal-carbon σ bonds can be cleaved by H_2 . Group IVA metal alkyls¹, e.g., Zr, react:



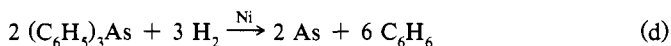
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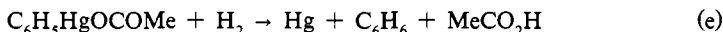
Cleavage of the hydrocarbon moieties from Pt or Os complexes occurs at $20^\circ C$, e.g.:



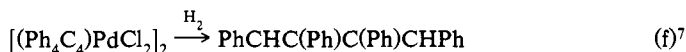
Triphenylarsine and Ph_3Bi with H_2 in the presence of Ni yield⁵ C_6H_6 , e.g.:



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Cleavage of π -bonded alkenes and alkynes from a metal complex can occur:

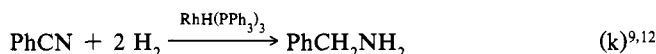
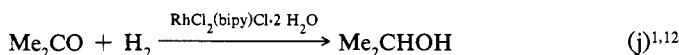
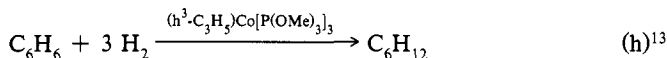


The formal cleavage of C—C bonds by H_2 in hydrogenolysis or cracking reactions, usually in the presence of metal catalysts⁸, e.g.:



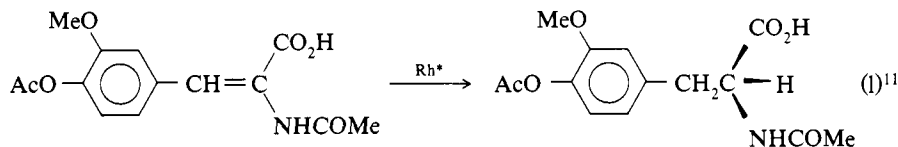
is common (see treatises on organic chemistry)⁹.

Homogeneous or heterogeneous catalyzed H_2 reduction of unsaturated organic compounds arene, alkyne, alkene, ketone, oxime, nitrile and imine occurs readily^{1,4,6,8-12}, e.g.:



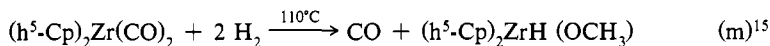
Hydrogenations using heterogeneous catalysts usually require above ambient T and H_2 pressures $\geq 10^3$ Pa. Homogeneous catalysts are often more selective and involve lower T (e.g., $25^\circ C$) and H_2 (ca. 10^2 Pa). Highly useful selectivity in hydrogenation is shown in reactions of H_2 with prochiral substrates in the presence of chiral catalysts, e.g., op-

tically active dopa, 3-(3,4-dihydroxyphenyl)-L-alanine, can be obtained in high optical purity (enantiomeric xs > 90%):



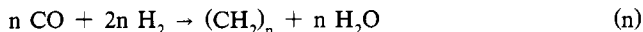
where $\text{Rh}^* = [\text{Rh}\{\text{S}\}(\text{S})\text{-}[\text{Ph}_2\text{P}(\text{Me})\text{C}_2\text{H}_2(\text{Me})\text{PPh}_2]](1,5\text{-C}_8\text{H}_{12})\text{Cl}$.

Reaction of H_2 with Zr-carbonyl complexes yields CH_3O -substituted products:



Under similar conditions the CO groups of the Ti complex, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$, are reduced to CH_4 ¹⁵.

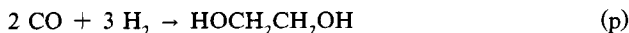
Reactions of H_2 with CO in the presence of catalysts produce hydrocarbon products ranging from CH_3OH and CH_4 to fuel oils¹⁶⁻²⁰:



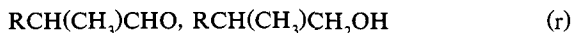
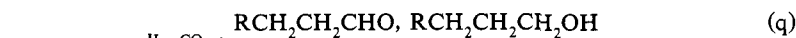
Products depend critically on reaction conditions. In the presence of $\text{Pd-La}_2\text{O}_3$ or $\text{Zn-Cr}_2\text{O}_3$, CO and H_2 form mainly CH_3OH :



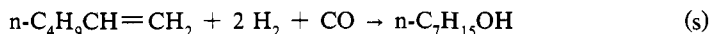
Over Ni at $500\text{--}700^\circ\text{C}$, CH_4 is the main product¹⁸. Other transition-metal heterogeneous catalysts produce higher yields of $\text{C} > 1$ products. Using the homogeneous catalyst, $\text{Rh}(\text{CO})_2(\text{MeCOCH}_2\text{CO}_2)$, $(\text{CH}_2\text{OH})_2$ forms in 70% yield¹⁹:



Hydroformylation, the addition of CO and H_2 to an olefin^{1,4,20}, occurs in the presence of homogeneous, $[\text{RhCl}(\text{PPh}_3)_3]$, $\text{HCo}(\text{CO})_4$, heterogeneous (Ni, Co, Fe, Rh) or supported catalysts $[\text{Rh}(\text{CO})_2\text{Cl}$ on $\text{SiO}_2]$ ^{18,20}:



Aldehydes form prior to alcohols, and both branched and linear isomers can arise; however, depending on the olefin substrate and under controlled reaction conditions, conditions highly specific for one compound often exist. From 1-hexene with an equimol CO and H_2 mixture at 5 to 9×10^3 Pa in $\text{EtOH-C}_6\text{H}_6$ at 110°C , in the presence of $\text{RhCl}_3(\text{PPh}_3)_3$, $n\text{-C}_7\text{H}_{15}\text{OH}$ forms nearly quantitatively¹:



Reaction of prochiral olefins with CO and H_2 in the presence of chiral catalysts results in asymmetric hydroformylation²¹.

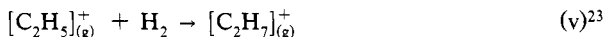
Carbon dioxide reacts with H_2 over a CuO-ZnO catalyst to form CH_3OH :



and over Ni to form CH_4 :



Hydrogen and $[\text{C}_2\text{H}_5]^+$ react in the gas phase to $[\text{C}_2\text{H}_7]^+$:



(A.D. NORMAN)

1. P. J. Brother, *Prog. Inorg. Chem.*, **28**, 1 (1981).
2. G. W. Parshall, *Adv. Organomet. Chem.*, **7**, 157 (1968).
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16. W. A. Hermann, *Angew. Chem., Int. Ed. Engl.*, **21**, 117 (1982).
17. E. Ramarson, R. Kieffer, A. Kiennemann, *J. Chem. Soc., Chem. Commun.*, 645 (1982).
18. G. A. Sommerjai, *Catal. Rev.-Sci. Eng.*, **23**, 189 (1981).
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22. J. Haggin, *Chem. Eng. News*, **60**, 13 (1982).
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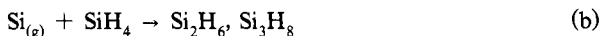
1.6.2.2. Giving Hydrides of Silicon.

Silicon at 400°C reacts with anhyd HCl yielding^{1,2} SiHCl_3 and SiCl_4 :



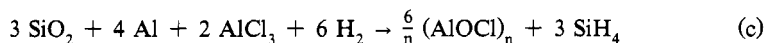
Similarly, alkylsilanes, e.g., MeSiCl_2H , are produced from the reaction of MeCl and H_2 with a hot Cu-Si mixture².

Ground-state Si^3P in the gas phase with SiH_4 yields Si_2H_6 , along with lesser amounts of Si_3H_8 through a combination of H abstraction and Si—H bond insertion³:



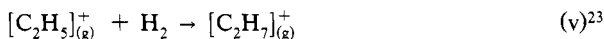
Silicon atoms in a matrix react above -196°C in the presence of Si—H bond-containing substrates (e.g., MeSiH_3 , Me_2SiH_2 , Me_3SiH , Si_2H_6) to form complex mixtures of products⁴. From the Si atom— Me_2SiH_2 reaction, a product mixture including CH_4 , $\text{Me}_2\text{Si}_2\text{H}_4$, $\text{Me}_3\text{Si}_2\text{H}_3$ and $\text{Me}_2\text{SiHSiH}_2\text{SiHMe}_2$ arises.

Hydrogen reacts with SiO_2 at 800°C in the presence of Al and AlCl_3 forming SiH_4 in high yield⁵. Optimum yields (ca. 80%) are attained with H_2 at 9×10^4 Pa.



68 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
1.6.2. from the Elements

Hydrogen and $[\text{C}_2\text{H}_5]^+$ react in the gas phase to $[\text{C}_2\text{H}_7]^+$:



(A.D. NORMAN)

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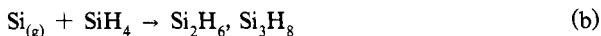
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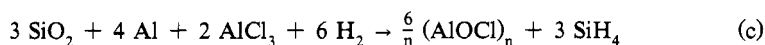
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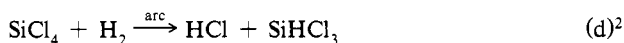


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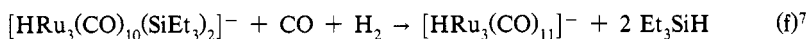
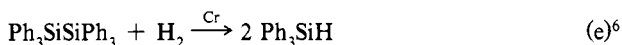


Hydrogen passed over Si at 1100–1200°C transports Si as a result of formation² of unstable SiH. Hydrogen reduces SiCl₄ to SiHCl₃ in a d.c. arc:



or to SiH₄ in an LiCl–KCl eutectic containing LiH. With the latter, reduction may involve LiH as the active species (see §1.6.4.2.1)².

Hydrogen or H₂–CO cleavage of Si–Si or Si–metal bonds can occur:



Atomic H reacts with SiH₄ in the gas phase, forming mixtures of silanes in low yield:



Silane is produced in low yields from reactions of at H with a Si surface²:

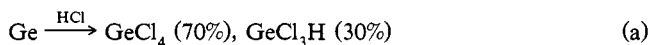


(A.D. NORMAN)

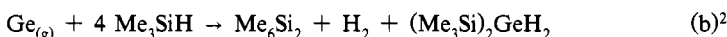
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1.6.2.3. Giving Hydrides of Germanium.

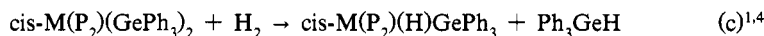
Germanium at 480–500°C reacts with anhyd HCl forming a mixture¹ of GeCl₃H and GeCl₄:



Tribromogermane is produced similarly in the reaction of HBr with Ge at 450°C in the presence of Cu powder. Trimethylsilane reacts with Ge atoms:



Hydrogen passed over liq Ge at 1000–1100°C transports Ge, probably through GeH₂ formation³. Hydrogen at 10² to 10⁴ Pa and 20–100°C cleaves the metal–Ge bonds in cis-Pt and -Pd complexes as:



where P₂ = 2 Et₃P, Ph₂PCH₂CH₂PPh₂; M = Pt, Pd.

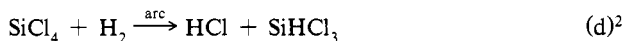
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1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 69

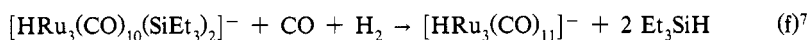
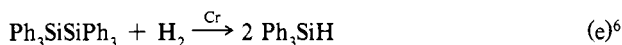
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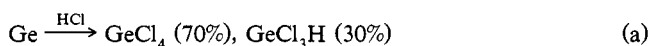


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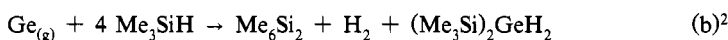
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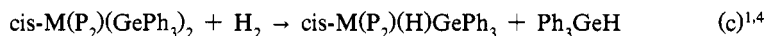
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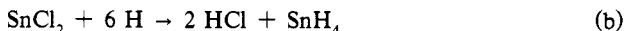
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Reactions of Sn, SnCl₂ or SnCl₄ with at H produce SnH₄:



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1.6.2.5. Giving Hydrides of Lead.

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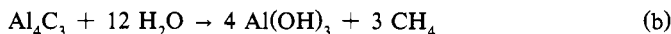
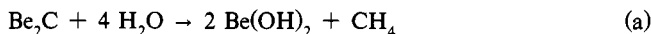
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1.6.3. by Group IVB Anionic Derivatives

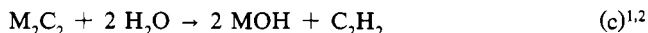
1.6.3.1. Giving Hydrides of Carbon

1.6.3.1.1. from Protonic Species in Water.

Carbides that in the solid contain discrete carbon anions yield hydrocarbons upon hydrolysis. Methanides of Be and Al hydrolyze forming^{1–3} CH₄:



The latter reaction is a preferred synthesis for laboratory quantities of CH₄. Hydrolysis of alkali, alkaline-earth and other electropositive metal (Cu, Ag, Au, Zn, Cd, Hg, Al) acetylides produces C₂H₂ in high yield, e.g.:



where M = Li, Na, K, Rb, Cs, Cu, Au.

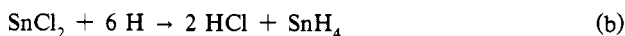
Hydrolysis of Mg₂C₃ yields CH₃C≡CH:

70 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb

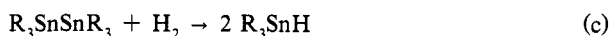
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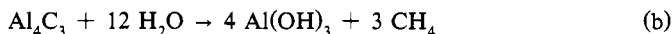
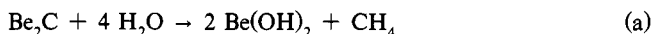


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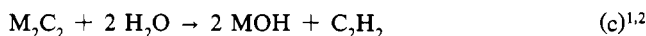
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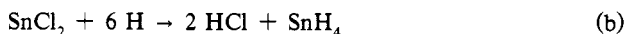
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70 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb

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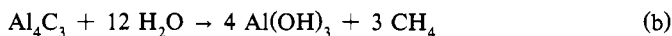
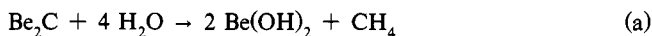


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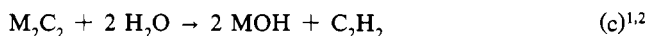
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where R = Me, Et, Ph; or Sn—Pt bonds, forming stannanes³:



(A.D. NORMAN)

1. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, 4, 1 (1968).
2. A. K. Sawyer, in *Organotin Compounds*, Vol. 3, A. K. Sawyer, ed., Marcel-Dekker, New York, 1971, p. 823.
3. D. M. Roundhill, *Adv. Organomet. Chem.*, 13, 273 (1975).

1.6.2.5. Giving Hydrides of Lead.

A highly reactive Pb film, formed by vapor deposition of Pb, reacts¹ with atomic H to form a Pb subhydride that decomposes to Pb and H₂ above 160°C:

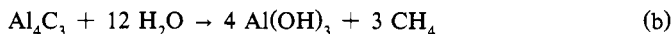
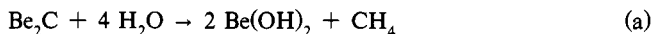


(A.D. NORMAN)

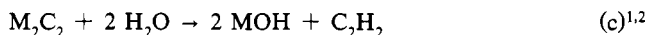
1. B. R. Wells, M. W. Roberts, *Proc. Chem. Soc.*, 173 (1964).

1.6.3. by Group IVB Anionic Derivatives**1.6.3.1. Giving Hydrides of Carbon****1.6.3.1.1. from Protonic Species in Water.**

Carbides that in the solid contain discrete carbon anions yield hydrocarbons upon hydrolysis. Methanides of Be and Al hydrolyze forming¹⁻³ CH₄:

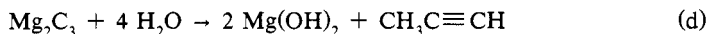


The latter reaction is a preferred synthesis for laboratory quantities of CH₄. Hydrolysis of alkali, alkaline-earth and other electropositive metal (Cu, Ag, Au, Zn, Cd, Hg, Al) acetylides produces C₂H₂ in high yield, e.g.:



where M = Li, Na, K, Rb, Cs, Cu, Ag, Au.

Hydrolysis of Mg₂C₃ yields CH₃C≡CH:

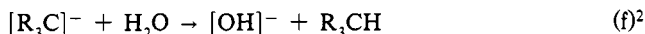


Lanthanide and actinide carbides with H_2O yield complex hydrocarbons mixtures. From ThC_2 in neutral H_2O , H_2 and $\text{C}_1\text{--C}_6$ hydrocarbons form¹ in % yields of: H_2 , 35; CH_4 , 4; C_2H_6 , 29; C_4H_{10} , 3; C_2H_4 , 5; C_4H_8 , 6; C_2H_2 , 8 and C_4H_4 , 4.

Cyanide ion reacts^{2,4} with H_2O forming the weak acid HCN ($\text{pK}_a = 4 \times 10^{-10}$):

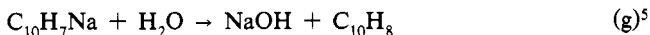


Protonation of resonance-stabilized carbanions occurs readily:

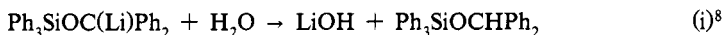


where $\text{R} = \text{CN}, \text{C}(\text{CN})_2, \text{NO}_2$.

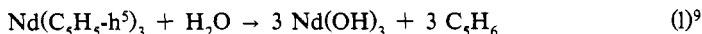
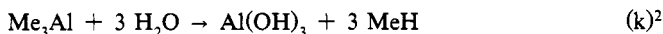
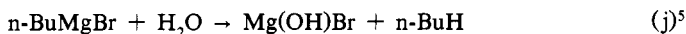
Metalated carbon compounds containing ionic, σ -covalent or partial σ -covalent bonds are hydrolyzed⁶ in reactions useful mainly for preparing D-containing compounds. Such reactions are highly preferred thermodynamically, because relatively strong C—H and metal–oxygen bonds are formed. Alkali-metal derivatives⁷ react, e.g.:



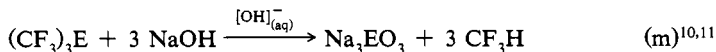
where $\text{R} = \text{Me}, \text{Et}, \text{i-Pr}, \text{n-Bu}, \text{t-Bu}$;



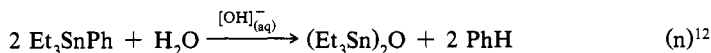
Other organometallic compounds, e.g., organo-Mg, Al, and Nd compounds, are hydrolyzed:



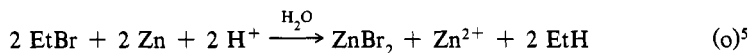
The fluorocarbon group VB (P, As, Sb, Bi) compounds are stable in H_2O , but are hydrolyzed in aqueous base:



where $\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$. Silicon, Ge and Sn compounds behave similarly. Aryl groups are removed in aqueous base; alkyl groups are not cleaved:

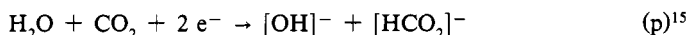


Active metal reduction of organic compounds in H_2O , e.g., alkyl halides with $\text{Zn}^{5,13}$, occurs:



Similar reduction of $[(\text{Me}_4\text{C})\text{NiCl}_2]_2$ produces $\text{Me}_4\text{C}_4\text{H}_4$ in 90% yield¹⁴.

Electrolytic reduction of CO_2 at an Hg cathode in H_2O yields the $[\text{HCO}_2]^-$ ion:



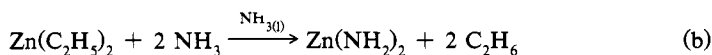
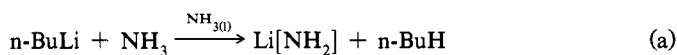
Numerous hydrolyses of unsaturated organic^{5,16} or organometallic intermediate species¹⁷ result in formation of C—H bonds (see treatises on organic synthetic chemistry).

(A.D. NORMAN)

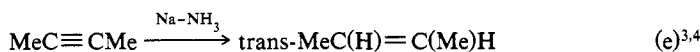
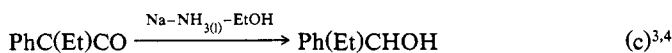
1. A. K. Holliday, G. Hughes, S. M. Walker, in *Comprehensive Inorganic Chemistry*, Vol. 1, A. F. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 1173.
2. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
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14. G. Burkhardt, H. Hoberg, *Angew. Chem., Int. Ed. Engl.*, 21, 76 (1982).
15. J. Ryu, T. N. Anderson, H. Eyring, *J. Phys. Chem.*, 76, 3278 (1972).
16. G. H. Whitham, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 1, J. F. Stoddart, ed., Pergamon Press, Oxford, 1979, p. 121.
17. A. E. Jukes, *Adv. Organomet. Chem.*, 12, 215 (1975).

1.6.3.1.2. from Protonic Species in Liquid Ammonia.

Reactions of electropositive metal alkyls with NH_3 in liq NH_3 yield the hydrocarbon and metal amide^{1,2}, in reactions more useful for the amide than for the hydrocarbon, e.g.:



Reductions of unsaturated organic molecules by alkali metals in liq NH_3 are used in organic syntheses^{3,4}, e.g.:

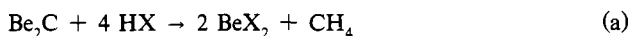


(A.D. NORMAN)

1. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
2. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
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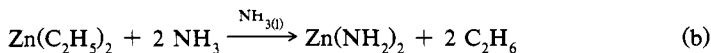
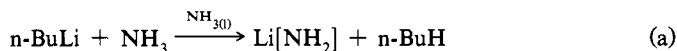


72 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.3. by Group IVB Anionic Derivatives
 1.6.3.1. Giving Hydrides of Carbon

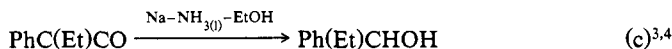
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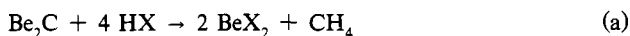


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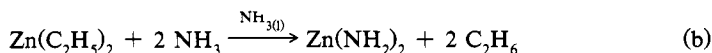
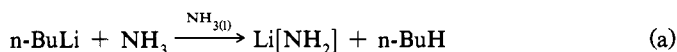


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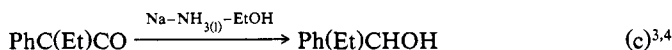
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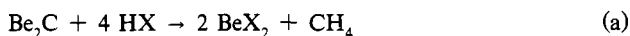


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Methanides react with protonic acids (HX) to form^{1,2} CH_4 , e.g.:



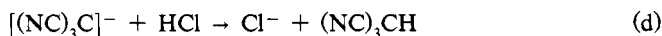
where X = Cl, Br, H₂PO₄, HSO₄, although CH₄ synthesis is better accomplished using H₂O (see §1.6.3.1.1). Acetylides and higher carbides¹ react similarly; however, subsequent reactions with the unsaturated products can occur. Carbide species formed in the gas phase, e.g., C⁻, C₂⁻ and C₄⁻, react with acidic substrates to form neutral molecules, which can further react to final products³:



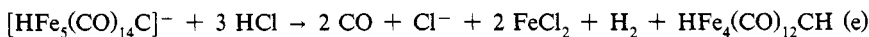
Protonic acids react with cyanide ion²:



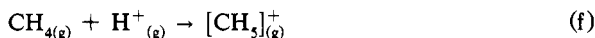
resonance- stabilized carbanions^{2,4}:



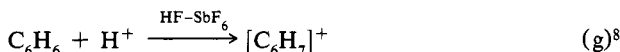
and an iron carbide cluster as:



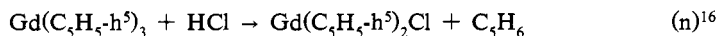
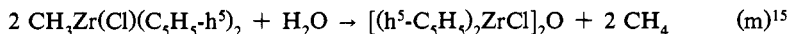
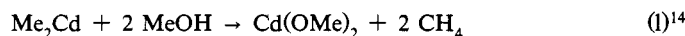
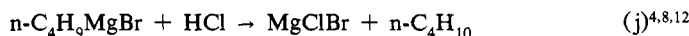
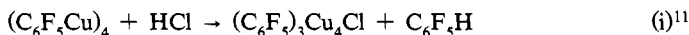
Protonation of hydrocarbons in the gas phase:



or in solution by strong acids results in carbocation formation^{4,6,7}:

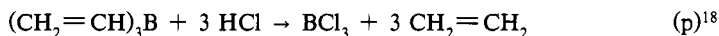


Organometallic compounds having varying degrees of carbanionic character are cleaved by protonic acids, e.g.:



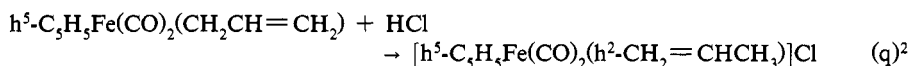
Reactions of compounds containing more than one R group proceed stepwise, allowing intermediate products to be obtained if a deficiency of HX is used [e.g., Eq. (i)]. Rates of bond scission vary also, usually the ease of cleavage is M-aryl > M-alkyl.

Cleavage of nonmetal element-C bonds with protonic acids can occur:

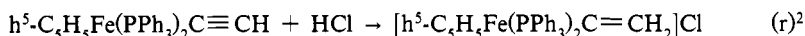


Such reactions can be important in syntheses (e.g., hydroboration) of hydrocarbons¹⁹.

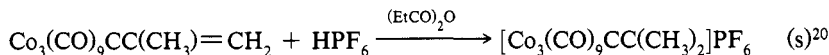
Organometallic complexes containing σ -bonded unsaturated moieties undergo protonation at the multiple bond. Reactions of HCl with σ -allylic complexes proceed as:



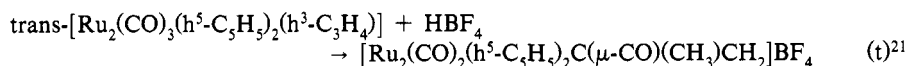
or with σ -alkynic complexes proceed as:



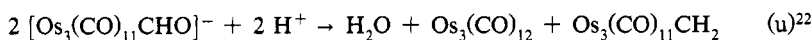
Strong-acid protonation of a σ -allylic Co_3 cluster yields the σ -alkyl cationic product:



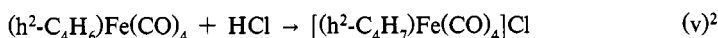
Protonation of bridging CH_2 groups in diruthenium complexes² proceeds:



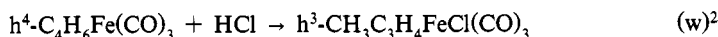
Formylate metal complexes can be converted to carbenes:



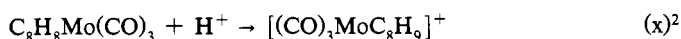
The $[(CO)_4Fe(HCO)]^-$ ion reacts to form H_2CO , in a reaction of undetermined stoichiometry²². Reaction of a π -complexed h^2 -butadiene-Fe complex with HCl occurs:



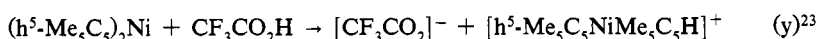
However, h^4 -dienes react to π -allyl (h^3) complexes:



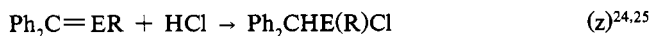
Cyclooctatetraene $\cdot Mo(CO)_3$ reacts with HCl to form a homotropylium ion complex:



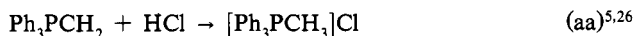
Trifluoroacetic acid protonates an $h^5-Me_5C_5$ group of $(h^5-Me_5C_5)_2Ni$:



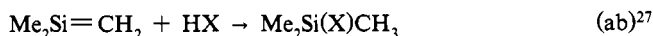
Protonation of nonmetal-C multiple bonds, in phosphaethyne or phospho- or arsaethenes:



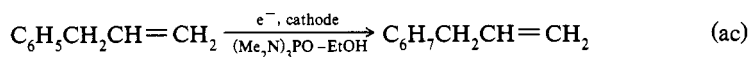
where $E = P, R = Cl$; $E = As, R = 2,4,6-Me_3C_6H_2$, yields C—H bonds. Phosphorus and arsenic ylids react similarly.



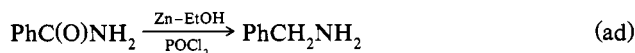
Species containing $Si=C$ bonds, formed as reaction intermediates, are added to by HX molecules:



where $X = OH, t-BuO, Cl$. Electrochemical cathodic reductions, e.g., of organohalides, carboxylic acids, alcohols or arenes proceed readily²⁸:



Active metal reductions, e.g., that of an amide, occur²⁹:



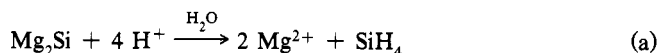
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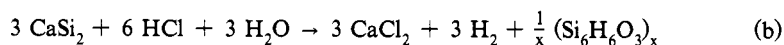
1.6.3.2. Giving Hydrides of Silicon

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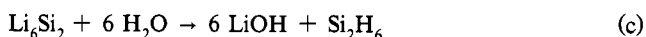
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1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 75

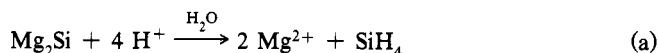
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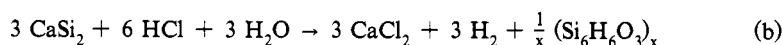
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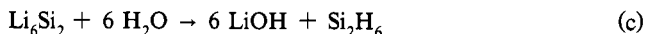
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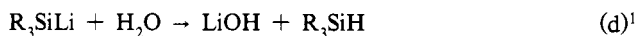


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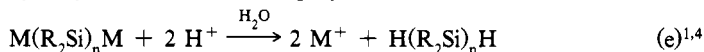


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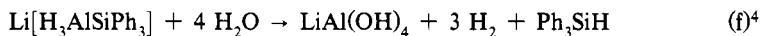
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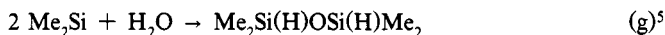
Polysilanes form in hydrolyses of dialkali-metal polysilicides:



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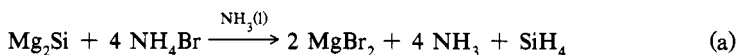
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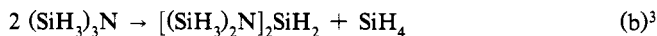
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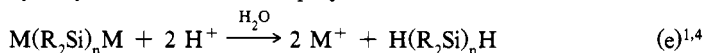
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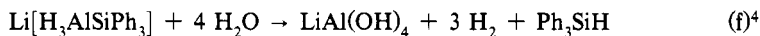
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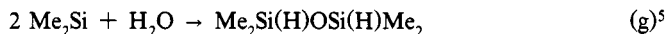
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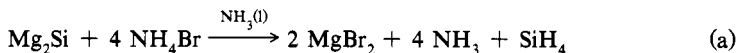
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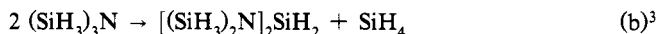
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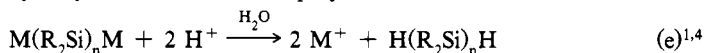
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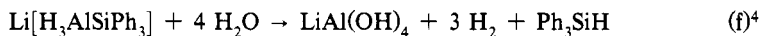
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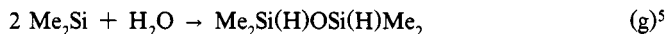
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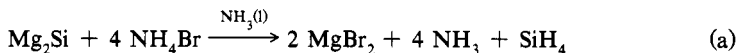
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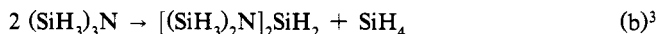
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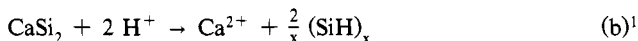
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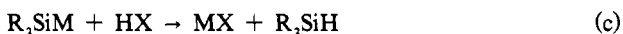


Calcium disilicide reacts with HCl in EtOH to form two-dimensional polysilanes as:

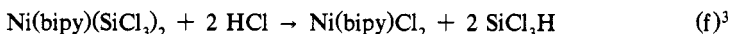
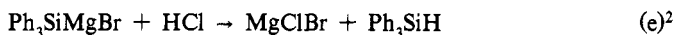
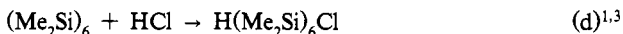


The ternary alloy $\text{Ca}(\text{Si}_{0.5}\text{Ge}_{0.5})$ with acid yields SiGeH_6 and SiGe_2H_8 , along with large quantities¹ of SiH_4 .

Protonation of alkali-metal silyl compounds produces the parent silanes in reactions that are useful for Si—D bond formation¹:



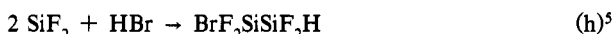
where R = H, alkyl, aryl; X = Cl, Br; M = Li, Na, K. Hydrogen-chloride cleavage of Si—Si or Si—metal bonds yields silanes:



Divalent silicon species react readily with protonic acids, e.g., Me_2Si from $(\text{Me}_2\text{Si})_6$ photolysis reacts with alcohols and amines:



where X = OMe, OEt, NEt_3 , n-BuO. Silicon difluoride reacts similarly with HBr above -196°C , forming a disilane:



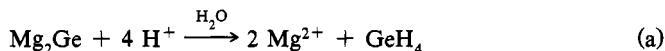
(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. Y. Kiso, K. Tamao, M. Kumada, *J. Organomet. Chem.*, **76**, 95 (1974).
3. P. G. Harrison, *Coord. Chem. Rev.*, **40**, 179 (1982).
4. K. P. Steele, W. P. Weber, *J. Am. Chem. Soc.*, **102**, 6095 (1980).
5. K. G. Sharp, J. F. Bald, *Inorg. Chem.*, **14**, 2553 (1975).

1.6.3.3. Giving Hydrides of Germanium

1.6.3.3.1. from Protonic Species in Water.

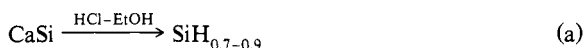
Protonation of Mg or Ca germanides or Mg-Ge alloys (Mg_2Ge) with acidic H_2O yields germanes of formula^{1,2} $\text{Ge}_n\text{H}_{2n+2}$. Germane forms from Mg_2Ge :



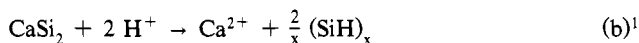
In practice a mixture of hydrides is obtained. Typically from the $\text{HCl}_{(\text{aq})}$ hydrolysis of Mg_2Ge arise¹, in % yield, GeH_4 , 15; Ge_2H_6 , 5; Ge_3H_8 , 5; Ge_4H_{10} , 1.5; Ge_5H_{12} , 0.8 and higher germanes (0.9%).

Ternary hydrides GeH_3PH_2 and GeH_3AsH_2 can be prepared from hydrolysis of $\text{CaGe-Ca}_3\text{P}_2$ or $\text{CaGe-Ca}_3\text{As}_2$, respectively². Similarly, Mg-Ge-Si alloys react with 10% HF in H_2O , forming mixtures of silanes, germanes, and ternary Si–Ge hydrides^{2,3}. From an alloy of nominal composition Mg_4SiGe is obtained the mixture, in % yield, SiGeH_6 , 0.6; SiGe_2H_8 , 0.4; n- $\text{SiGe}_3\text{H}_{10}$, 0.03; n- $\text{Si}_2\text{Ge}_2\text{H}_{10}$, 0.5 and n- $\text{Si}_3\text{Ge}_2\text{H}_{12}$.

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 77
 1.6.3. by Group IVB Anionic Derivatives

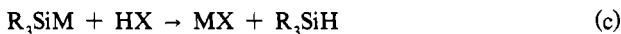


Calcium disilicide reacts with HCl in EtOH to form two-dimensional polysilanes as:

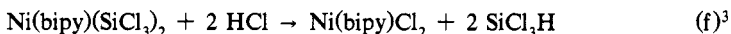
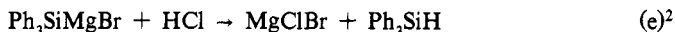
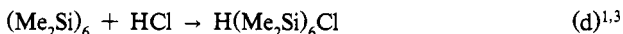


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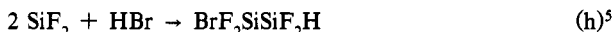
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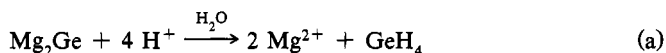
(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
2. Y. Kiso, K. Tamao, M. Kumada, *J. Organomet. Chem.*, **76**, 95 (1974).
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4. K. P. Steele, W. P. Weber, *J. Am. Chem. Soc.*, **102**, 6095 (1980).
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1.6.3.3. Giving Hydrides of Germanium

1.6.3.3.1. from Protonic Species in Water.

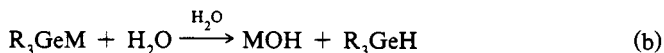
Protonation of Mg or Ca germanides or Mg-Ge alloys (Mg_2Ge) with acidic H_2O yields germanes of formula^{1,2} $\text{Ge}_n\text{H}_{2n+2}$. Germane forms from Mg_2Ge :



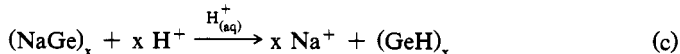
In practice a mixture of hydrides is obtained. Typically from the $\text{HCl}_{(\text{aq})}$ hydrolysis of Mg_2Ge arise¹, in % yield, GeH_4 , 15; Ge_2H_6 , 5; Ge_3H_8 , 5; Ge_4H_{10} , 1.5; Ge_5H_{12} , 0.8 and higher germanes (0.9%).

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Hydrolysis of alkali-metal alkyl- or arylgermanides yields the corresponding Ge hydrides in reactions most useful for Ge—D bond formation⁴:



where M = Li, Na, K; R = Ph, PhCH₂, Et, etc. Treatment of sodium germanide (NaGe) with aqueous acid yields a polymeric Ge subhydride¹:

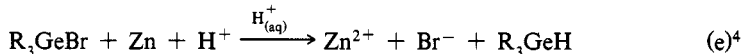


Germylmagnesium halides are hydrolyzed easily to the parent germanes:



where R = Et, i-Pr; C₆H₁₁, Ph, etc.

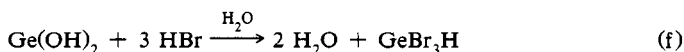
Active metal reduction (Zn, Mg or Zn amalgam) of trialkyl- and triarylgermanium halides or (Me₂GeS)₂ in aq acid yields the respective germanes, e.g.:



where R = Me, Et, Ph. Sodium amalgam, Zn, or Mg reductions of Ge(IV) species in aq sulfuric acid produce GeH₄ in low yields².

Electrolytic reduction of aq alkaline [GeO₃]²⁻ solns or Ph₂GeCl₂ produces GeH₄² or Ph₂GeH₂⁵, respectively, in low yields.

Hydrolysis of SiO—GeO mixtures produces silanes, germanes, and ternary Si—Ge hydrides². Germanium(II) hydroxide with aq HBr yields⁴ GeBr₃H:



Acid hydrolysis of KGeH₃BH₃ or KGeH₃BMe₃ produces GeH₄ in high yield⁶:



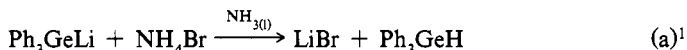
Cleavage of the Ge—C bond in GeH₃CO₂H by acetic acid, followed by decarbonylation, yields CO, GeH₄ and a Ge subhydride⁷.

(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
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5. R. E. Dessey, W. Kitching, T. Chivers, *J. Am. Chem. Soc.*, **88**, 453 (1966).
6. E. R. DeStaruco, C. Riddle, W. L. Jolly, *J. Inorg. Nucl. Chem.*, **35**, 297 (1973).
7. P. G. Harrison, *Coord. Chem. Rev.*, **30**, 137 (1979).

1.6.3.3.2. from Protonic Species in Liquid Ammonia.

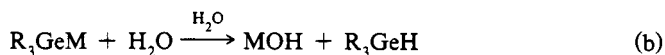
Protonation of alkyl- or aryl-substituted germanides in NH_{3(l)} by NH₄Br produces germanes in high yields:



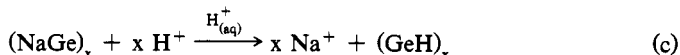
Trialkylgermanides react similarly; however, being more basic they react directly with NH₃:

78 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.3. by Group IVB Anionic Derivatives
 1.6.3.3. Giving Hydrides of Germanium

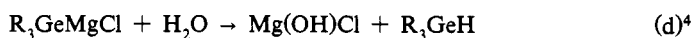
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where M = Li, Na, K; R = Ph, PhCH₂, Et, etc. Treatment of sodium germanide (NaGe) with aqueous acid yields a polymeric Ge subhydride¹:

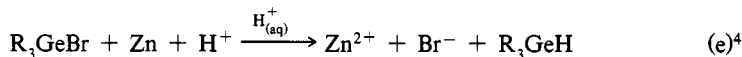


Germylmagnesium halides are hydrolyzed easily to the parent germanes:



where R = Et, i-Pr; C₆H₁₁, Ph, etc.

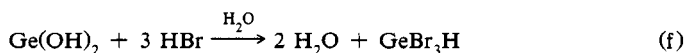
Active metal reduction (Zn, Mg or Zn amalgam) of trialkyl- and triarylgermanium halides or (Me₂GeS)₂ in aq acid yields the respective germanes, e.g.:



where R = Me, Et, Ph. Sodium amalgam, Zn, or Mg reductions of Ge(IV) species in aq sulfuric acid produce GeH₄ in low yields².

Electrolytic reduction of aq alkaline [GeO₃]²⁻ solns or Ph₂GeCl₂ produces GeH₄² or Ph₂GeH₂⁵, respectively, in low yields.

Hydrolysis of SiO—GeO mixtures produces silanes, germanes, and ternary Si—Ge hydrides². Germanium(II) hydroxide with aq HBr yields⁴ GeBr₃H:



Acid hydrolysis of KGeH₃BH₃ or KGeH₃BMe₃ produces GeH₄ in high yield⁶:



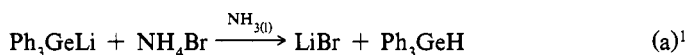
Cleavage of the Ge—C bond in GeH₃CO₂H by acetic acid, followed by decarbonylation, yields CO, GeH₄ and a Ge subhydride⁷.

(A.D. NORMAN)

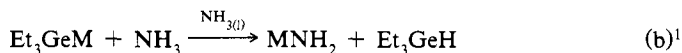
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1.6.3.3.2. from Protonic Species in Liquid Ammonia.

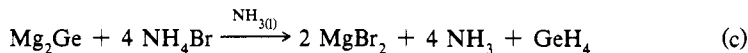
Protonation of alkyl- or aryl-substituted germanides in NH_{3(l)} by NH₄Br produces germanes in high yields:



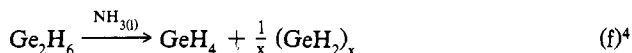
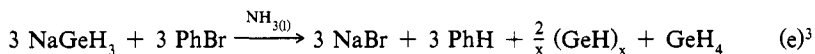
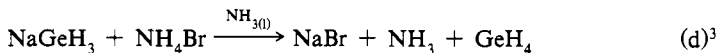
Trialkylgermanides react similarly; however, being more basic they react directly with NH₃:



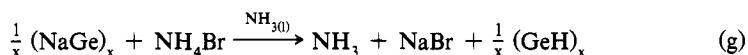
Ammonium bromide protonation of Mg_2Ge in $\text{NH}_{3(l)}$ yields GeH_4 (60–70% yield), with only small quantities of higher hydrides²:



Reactions of GeH_4 derivatives or Ge_2H_6 in $\text{NH}_{3(l)}$ result in GeH_4 and sometimes Ge subhydrides:



Sodium germanide (NaGe) protonation by NH_4Br yields³ $(\text{GeH})_x$:



Electrolysis of NaGeH_3 in $\text{NH}_{3(l)}$ using a Pt anode and an Hg cathode produces small quantities⁵ of GeH_4 .

(A.D. NORMAN)

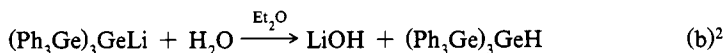
1. M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971.
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1.6.3.3.3. from Protonic Acids in Other Solvents.

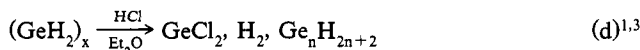
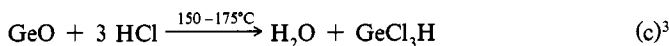
Protonation of germanides by hydrogen halides, water or alcohols in nonprotonic solvents yields the parent germanes, e.g.^{1,2}:



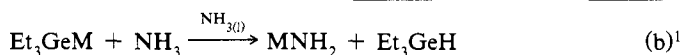
where R = H, alkyl, aryl; X = Cl, Br; M = Li, Na, K;



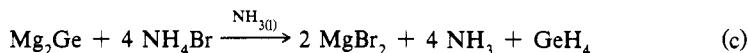
Hydrogen halides add to Ge(II) hydrides, halides, oxides or sulfides:



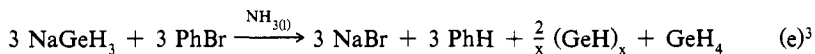
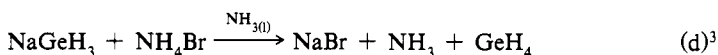
1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 79
 1.6.3. by Group IVB Anionic Derivatives
 1.6.3.3. Giving Hydrides of Germanium



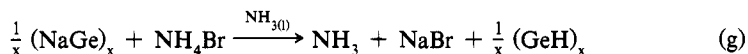
Ammonium bromide protonation of Mg_2Ge in $\text{NH}_{3(0)}$ yields GeH_4 (60–70% yield), with only small quantities of higher hydrides²:



Reactions of GeH_4 derivatives or Ge_2H_6 in $\text{NH}_{3(0)}$ result in GeH_4 and sometimes Ge subhydrides:



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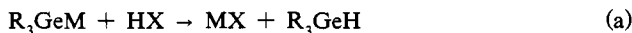
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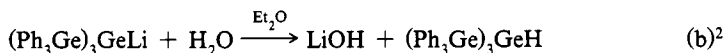
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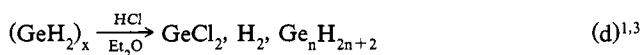
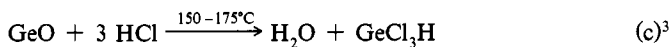
Protonation of germanides by hydrogen halides, water or alcohols in nonprotonic solvents yields the parent germanes, e.g.^{1,2}:



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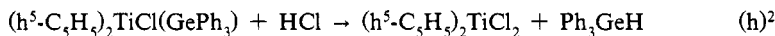
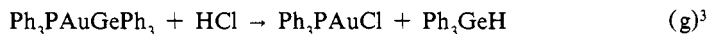
Hydrogen halides add to Ge(II) hydrides, halides, oxides or sulfides:



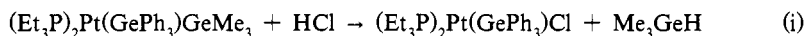
Protonic acid cleavage of metal–Ge bonds when the electronegativity of Ge exceeds that of the metal results in germane formation, e.g.:



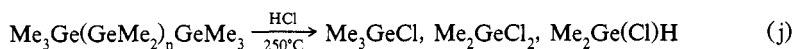
Reaction of $\text{Ph}_3\text{PAuGePh}_3$ with HCl yields Ph_3GeH :



In an unsymmetrically substituted germylplatinum compound one equiv of HCl selectively cleaves the Me_3Ge group²:



Hydrogen-chloride cleavage of Ge—Ge bonds in polymethylated germanes yields a mixture of methylgermanes², including $\text{Me}_2\text{Ge}(\text{Cl})\text{H}$:



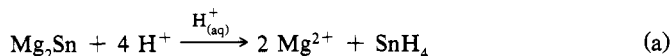
(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971.
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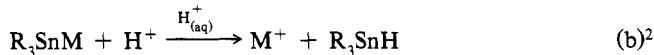
1.6.3.4. Gring Hydrides of Tin

1.6.3.4.1. from Protonic Species in Water.

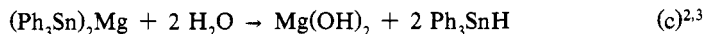
Stannane forms in low yields from the aq HCl or H_2SO_4 hydrolysis of Mg–Sn alloy¹:



Metal triorganostannides ($\text{R} = \text{Et}$, $n\text{-Bu}$, Ph , etc.) are hydrolyzed to the parent stannanes. Alkali-metal derivatives react:



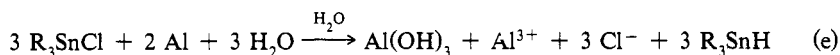
where $\text{R} = n\text{-Bu}$, Ph ; $\text{M} = \text{Li}$, Na . Hydrolysis of Mg derivatives, e.g., produces triorganostannanes in high yield:



Triethylstannane results from hydrolysis of $\text{Et}_3\text{Sn}(\text{Me}_2\text{N})_2\text{B}$:



Aluminum amalgam reduction of triorganochlorostannanes forms the hydrides in < 60% yields²:



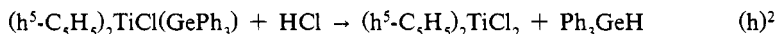
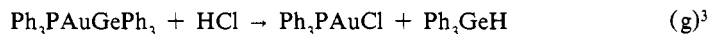
Dichloro- and trichlorostannanes are reduced less efficiently. Stannane is obtained⁴

80 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.3. by Group IVB Anionic Derivatives

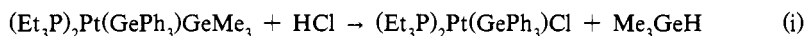
Protonic acid cleavage of metal-Ge bonds when the electronegativity of Ge exceeds that of the metal results in germane formation, e.g.:



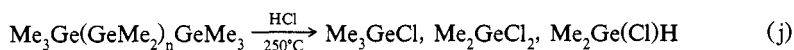
Reaction of $\text{Ph}_3\text{PAuGePh}_3$ with HCl yields Ph_3GeH :



In an unsymmetrically substituted germlyplatinum compound one equiv of HCl selectively cleaves the Me_3Ge group²:



Hydrogen-chloride cleavage of Ge-Ge bonds in polymethylated germanes yields a mixture of methylgermanes², including $\text{Me}_2\text{Ge}(\text{Cl})\text{H}$:



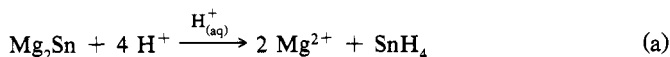
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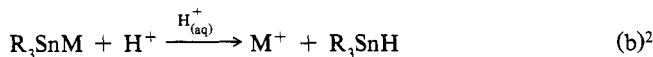
1.6.3.4. Gring Hydrides of Tin

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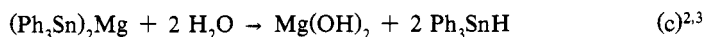
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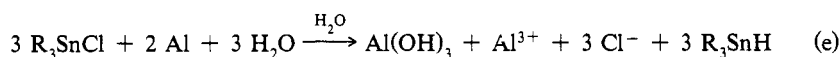
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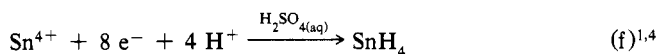


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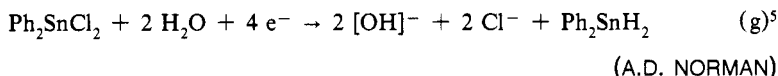


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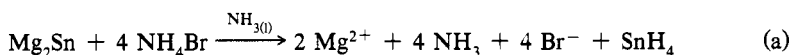
or Ph_2SnH_2 , respectively:



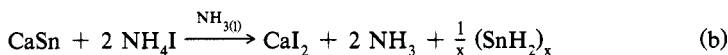
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1.6.3.4.2. from Protonic Species in Liquid Ammonia.

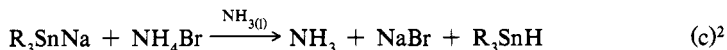
Ammonium bromide protonation of Mg_2Sn in liq NH_3 yields SnH_4 , although inefficiently¹:



Calcium stannide with NH_4I in $\text{NH}_{3(\text{l})}$ form a solid polystannane¹:



Reaction of Na triorganostannides with NH_4Cl or NH_4Br in $\text{NH}_{3(\text{l})}$ yields the corresponding stannanes:



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

(A.D. NORMAN)

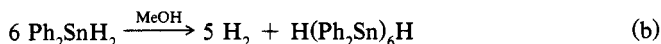
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1.6.3.4.3. from Protonic Species in Other Solvents.

Protonation of organostannides in aprotic solvents yields stannanes¹. Protonation of R_2Sn species with HCl or $[\text{NH}_4][\text{HF}_2]$ occurs:



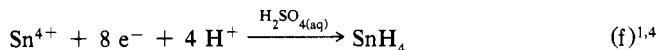
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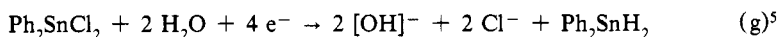
(A.D. NORMAN)

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 81
 1.6.3. by Group IVB Anionic Derivatives
 1.6.3.4. Giving Hydrides of Tin

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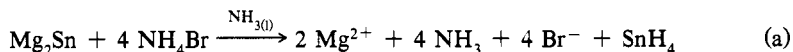


(A.D. NORMAN)

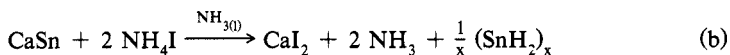
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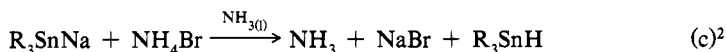
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where R = Me, Et, Ph.

(A.D. NORMAN)

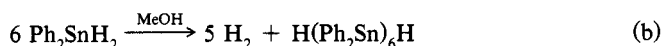
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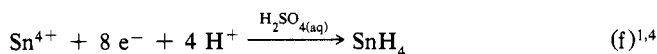


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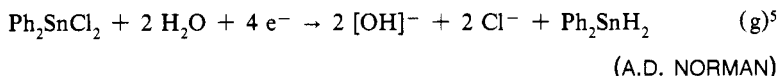


(A.D. NORMAN)

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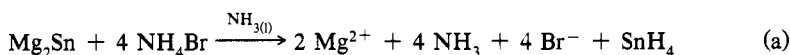
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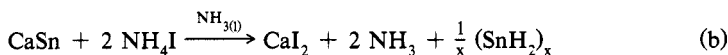
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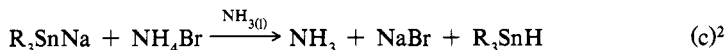
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(A.D. NORMAN)

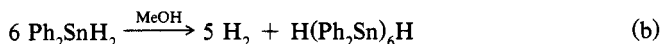
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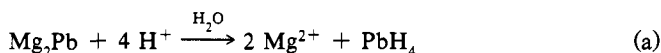


(A.D. NORMAN)

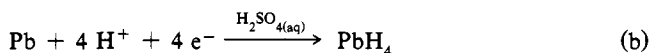
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1.6.3.5. Giving Hydrides of Lead.

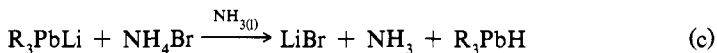
Traces of PbH_4 form in reactions of Mg-Pb alloy with aq acid¹:



or in the electrochemical reduction of lead anodes²:



Aluminum-foil reduction of $\text{MPb}(\text{OH})_3$ (M = alkali metals) in H_2O yields a solid Pb subhydride, Pb_2H_2 , which decomposes in vacuum². Trialkyl- and triarylplumbides with NH_4Br in $\text{NH}_{3(0)}$ form plumbanes in low yield³:



where R = Et, Ph, C_6H_{11} .

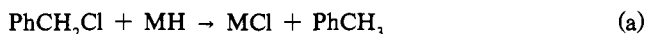
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1.6.4. by Hydride Reduction

1.6.4.1. Giving Hydrides of Carbon

1.6.4.1.1. from Halides.

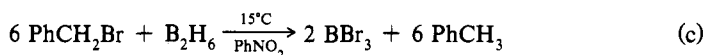
Binary ionic or covalent hydride reduction of organic halides is important in organic syntheses^{1,2}. Reactions of metal hydrides with alkyl halides in ethers occur:



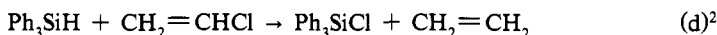
where M = Li, Na, K. Sodium hydride with aryl iodides forms the parent arenes²:



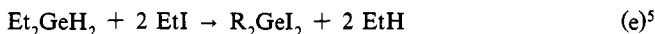
Diborane reacts only slowly with most alkyl halides³; however, reduction of PhCH_2Br occurs readily⁴ in PhNO_2 :



Organosilanes, at elevated T (ca. 600°C) or with catalysts, (Pd on C), react:



Organogermane and organostannane reductions occur under milder conditions:

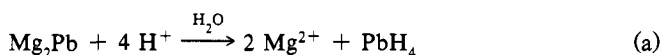


82 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb

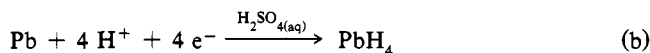
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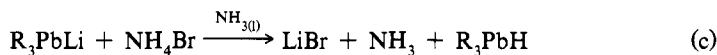
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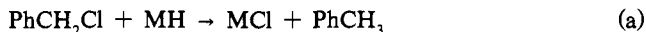


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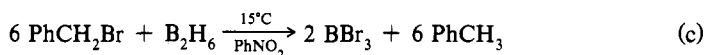
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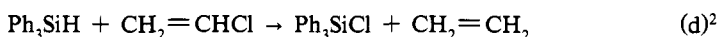
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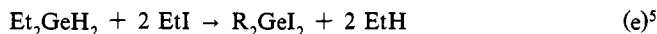
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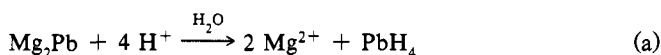


82 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb

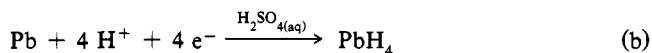
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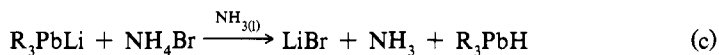
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or in the electrochemical reduction of lead anodes²:



Aluminum-foil reduction of $\text{MPb}(\text{OH})_3$ (M = alkali metals) in H_2O yields a solid Pb subhydride, Pb_2H_2 , which decomposes in vacuum². Trialkyl- and triarylplumbides with NH_4Br in $\text{NH}_{3(0)}$ form plumbanes in low yield³:

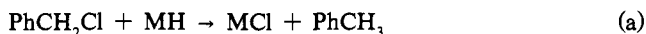


where R = Et, Ph, C_6H_{11} .

1. F. E. Saalfeld, H. J. Svec, *Inorg. Chem.*, 2, 46 (1963).
2. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.

1.6.4. by Hydride Reduction**1.6.4.1. Giving Hydrides of Carbon****1.6.4.1.1. from Halides.**

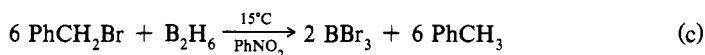
Binary ionic or covalent hydride reduction of organic halides is important in organic syntheses^{1,2}. Reactions of metal hydrides with alkyl halides in ethers occur:



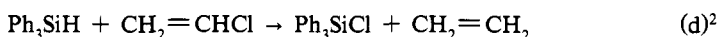
where M = Li, Na, K. Sodium hydride with aryl iodides forms the parent arenes²:



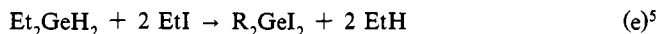
Diborane reacts only slowly with most alkyl halides³; however, reduction of PhCH_2Br occurs readily⁴ in PhNO_2 :

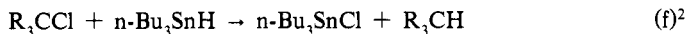


Organosilanes, at elevated T (ca. 600°C) or with catalysts, (Pd on C), react:



Organogermane and organostannane reductions occur under milder conditions:





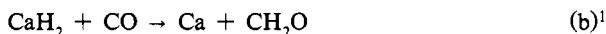
Stannanes supported on SiO_2 or Al_2O_3 reduce alkyl halides cleanly to alkanes in 40% yields⁶.

(A.D. NORMAN)

1. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961.
2. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
3. C. H. Long, *Adv. Inorg. Chem. Radiochem.*, 16, 201 (1974).
4. S. Matsumura, N. Takura, *Tetrahedron Lett.*, 363 (1969).
5. M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Chemistry of Germanium*, Wiley-Interscience, New York, 1971.
6. H. Schuman, B. Pachaly, *Angew. Chem., Int. Ed. Engl.*, 20, 1043 (1981).

1.6.4.1.2. from Oxygen Compounds.

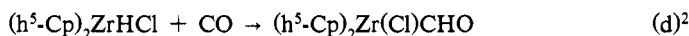
Carbon monoxide reacts with CaH_2 at high T ($> 600^\circ\text{C}$) to form CH_4 and small quantities of CH_2O :



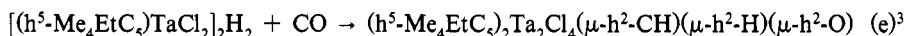
Reaction with KH at $240\text{--}270^\circ\text{C}$ yields formate ion¹:



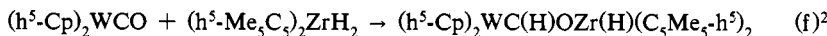
Zirconium and Ta hydride complexes react with CO forming formyl:



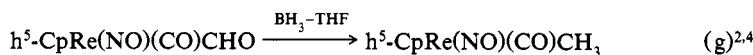
and $\mu\text{-CH}$ complexes:



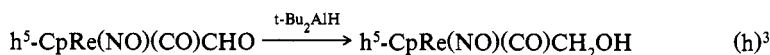
Tungsten-coordinated CO reacts with $(\text{h}^5\text{-Me}_5\text{C}_5)_2\text{ZrH}_2$:



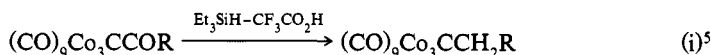
Reduction of formyl or acyl metal complexes with BH_3 :



$t\text{-Bu}_2\text{AlH}$:



or Et_3SiH :

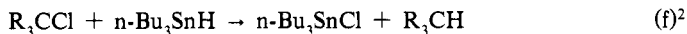


where $\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{Ph}$, proceeds easily.

Alkali-metal hydrides ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and CO_2 yield metal formates in reactions that normally require elevated T:



1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb	83
1.6.4. by Hydride Reduction	
1.6.4.1. Giving Hydrides of Carbon	



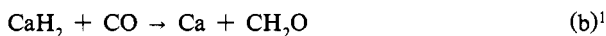
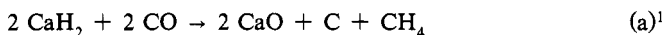
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4. S. Matsumura, N. Takura, *Tetrahedron Lett.*, 363 (1969).
5. M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Chemistry of Germanium*, Wiley-Interscience, New York, 1971.
6. H. Schuman, B. Pachaly, *Angew. Chem., Int. Ed. Engl.*, 20, 1043 (1981).

1.6.4.1.2. from Oxygen Compounds.

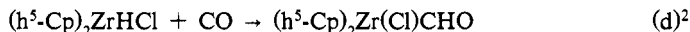
Carbon monoxide reacts with CaH_2 at high T ($> 600^\circ C$) to form CH_4 and small quantities of CH_2O :



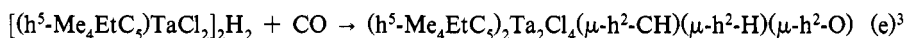
Reaction with KH at $240-270^\circ C$ yields formate ion¹:



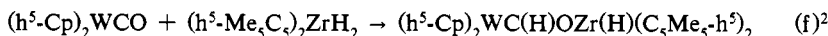
Zirconium and Ta hydride complexes react with CO forming formyl:



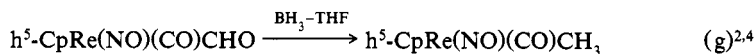
and μ -CH complexes:



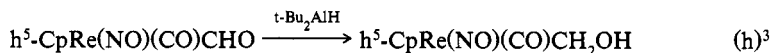
Tungsten-coordinated CO reacts with $(h^5-Me_5C_5)_2ZrH_2$:



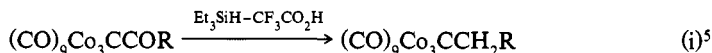
Reduction of formyl or acyl metal complexes with BH_3 :



$t-Bu_2AlH$:



or Et_3SiH :

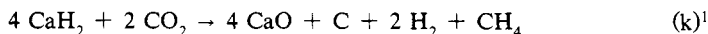


where R = Me, Et, i-Pr, Ph, proceeds easily.

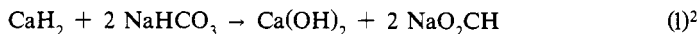
Alkali-metal hydrides (M = Li, Na, K) and CO_2 yield metal formates in reactions that normally require elevated T:



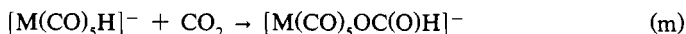
Calcium hydride and CO_2 or NaHCO_3 produce CH_4 :



or $\text{NaO}_2\text{CH}^{1,2}$:



Group VIA metal-carbonyl hydrides react with CO_2 or COS , forming metalloformate:



where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, or thioformate complexes⁶.

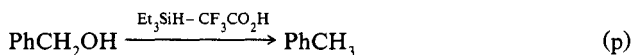
Binary hydride (boranes, alanes, silanes, stannanes) reductions of oxygen-containing compounds are used in organic synthesis⁷⁻⁹, e.g., with ketones :



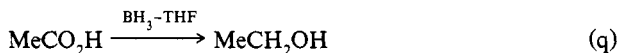
aldehydes:



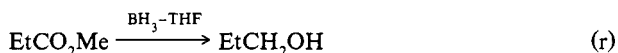
alcohols:



carboxylic acids:



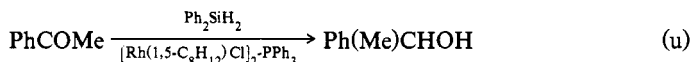
and esters:



The final products shown are obtained after hydrolysis of intermediate addition species, e.g.:

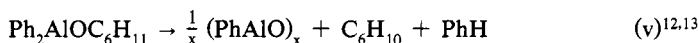


Variation of substituent groups and reaction conditions allows considerable reaction selectivity, as in:

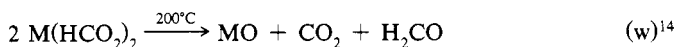


where Ph_2SiH_2 in the presence of a chiral catalyst reduces PhCOMe to chiral product in 57% optical yield^{10,11}.

Thermolysis of alkoxymetal compounds often yields alkanes, e.g.:



Metal carboxylates decarboxylate upon heating:

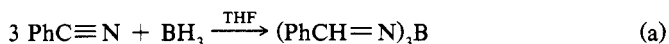


(A.D. NORMAN)

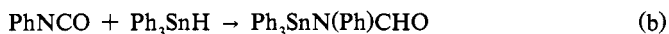
1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. J. A. Gladysz, *Adv. Organomet. Chem.*, **20**, 1, (1982).
3. M. R. Churchill, H. J. Wasserman, *J. Chem. Soc., Chem. Commun.*, 274 (1981).
4. C. Master, *Adv. Organomet. Chem.*, **17**, 61 (1979).
5. D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).
6. D. J. Darensbourg, A. Rokicki, *J. Am. Chem. Soc.*, **104**, 349 (1982).
7. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961. Comprehensive treatment of organic syntheses and reactions.
8. H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972. Basic, readable review of borane reductions.
9. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979. Excellent summary of hydrides in organic reductions.
10. H. Brunner, G. Riepl, *Angew. Chem., Int. Ed. Engl.*, **21**, 377 (1982).
11. D. M. Roundhill, *Adv. Organomet. Chem.*, **13**, 273 (1975).
12. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
13. E. C. Ashby, G. F. Willard, A. B. Goel, *J. Org. Chem.*, **44**, 1221 (1979).
14. M. N. Ray, N. D. Sinnarka, *J. Inorg. Nucl. Chem.*, **35**, 1373 (1973).

1.6.4.1.3. from Nitrogen Compounds.

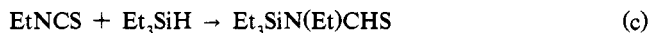
Boranes, alanes, silanes, germanes and stannanes, and their substituted derivatives, reduce C—N multiple bonds^{1–3}, e.g., with nitriles:



cyanates:



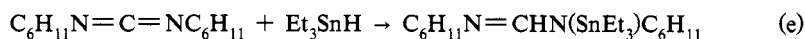
thiocyanates:



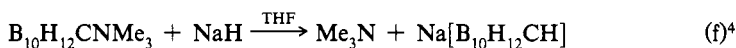
imines:



and carbodimides:



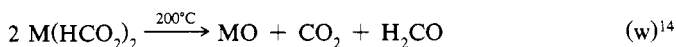
Reaction of NaH with the zwitterionic ammonium carboranes results in cleavage of the NMe₃ moiety and formation of the anionic carborane product:



(A.D. NORMAN)

1. H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972.
2. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
3. C. A. Beuhler, D. E. Pearson, *Organic Syntheses*, Vol. 2, Wiley-Interscience, New York, 1977.
4. D. E. Hyatt, F. R. Scholer, L. J. Todd, J. L. Warner, *Inorg. Chem.*, **6**, 2229 (1967).

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 85
 1.6.4. by Hydride Reduction
 1.6.4.1. Giving Hydrides of Carbon

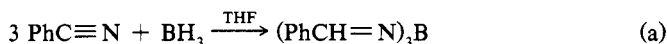


(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
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1.6.4.1.3. from Nitrogen Compounds.

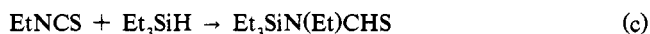
Boranes, alanes, silanes, germanes and stannanes, and their substituted derivatives, reduce C—N multiple bonds¹⁻³, e.g., with nitriles:



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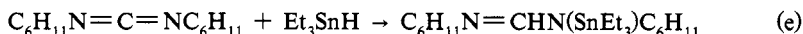
thiocyanates:



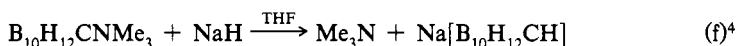
imines:



and carbodimides:



Reaction of NaH with the zwitterionic ammonium carboranes results in cleavage of the NMe₃ moiety and formation of the anionic carborane product:



(A.D. NORMAN)

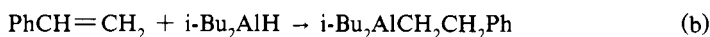
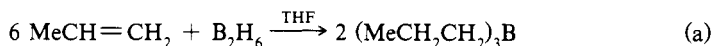
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- 86 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.4. by Hydride Reduction
 1.6.4.1. Giving Hydrides of Carbon

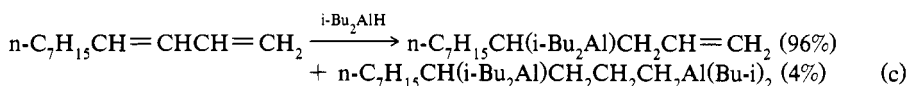
1.6.4.1.4. from Compounds with Carbon–Carbon Multiple Bonds.

Group IIIB (B, Al), IVB (Si, Ge, Sn, Pb), VB (P, As, Sb) and VIB (S, Se) hydrides add to C=C or C≡C bonds under thermal, photolytic, radical-initiated and catalyzed (homogeneous or heterogeneous) conditions. Such reactions are routes to alkyl- or alkenyl-element compounds and to intermediates subsequent to hydrolyzed or reduced products. Addition places the hydrogen on the carbon with least hydrogen, except under highly polar-reagent addition (e.g., base-catalyzed) conditions, where hydrogen adds to the carbon with most hydrogens.

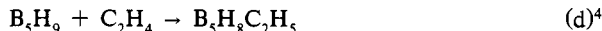
Group IIIB hydrides^{1,2} react thermally, e.g.:



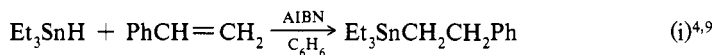
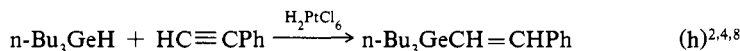
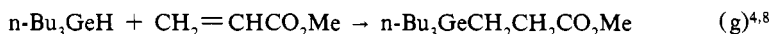
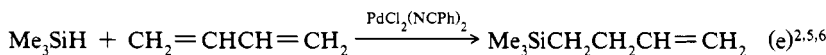
Reactions can be highly selective. Excess $i\text{-Bu}_2\text{AlH}$ reacts with $n\text{-C}_7\text{H}_{15}\text{CH=CH-CH=CH}_2$ almost quantitatively first at the more highly substituted C=C bond. Only 4% reaction with the terminal C=C bond occurs³:



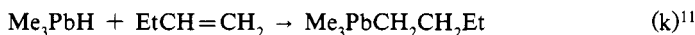
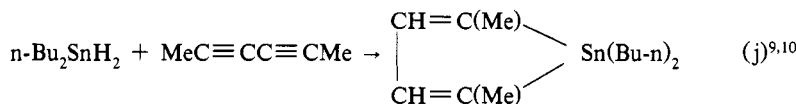
Boranes (B > 1) react with olefins and alkynes, e.g.:



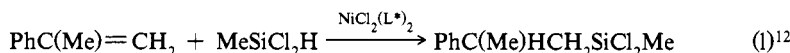
Group IVB hydrides react with alkynes and alkenes under thermal, photolytic, radical-initiated and catalyzed (homogeneous or heterogeneous) conditions^{2,4}, e.g.:



where AIBN = 2,2'-[Me₂(CN)C]₂N₂;

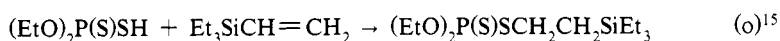
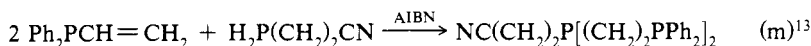


By variation of substituents, reactivity of the hydride toward C=C or C≡C bonds can be modified. Asymmetric reduction of prochiral olefins², in the presence of chiral catalysts can be achieved. Reaction of styrene:

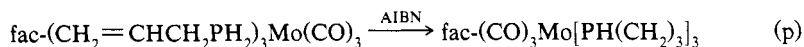


where $L^* = (R)-PhCH_2(Me)(Ph)P$, after hydrolysis to products, yields $PhC(Me)HCH_3$ in optical purity up to 18%.

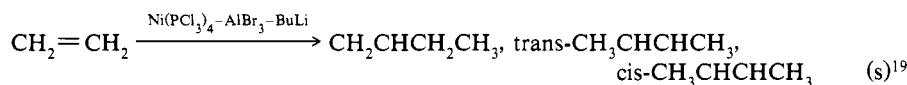
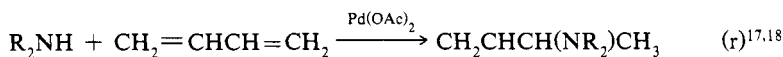
Group VB and VIB hydrides react with alkenes and alkynes, thermally or under radical, photolytic or base catalysis, in reactions used primarily for substituted element (P, As, Sb) compound synthesis, e.g.:



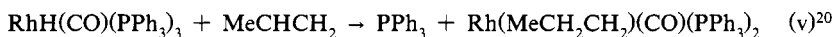
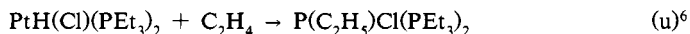
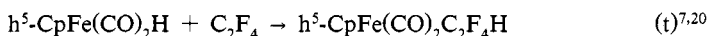
Metal-coordinated phosphines react similarly, as in the metal-templated cyclization¹⁶ of $(CO)_3Mo(PH_2CH_2CH=CH_2)_3$ in the presence of 2,2'-azobis(isobutyronitrile)(AIBN):



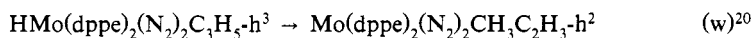
Numerous organic synthetic reactions^{17,18} occur, e.g.:



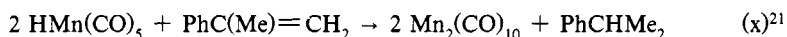
Transition-metal hydrides react with olefins to form σ -bonded derivatives:



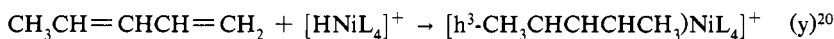
Both addition of hydrogen to carbon with the most hydrogens in unsymmetrical olefins and its reverse can occur²⁰. Intramolecular hydride transfer, e.g., in $HMo(dppe)_2-(N_2)_2C_3H_5-h^3$, produces the h^2 -propene:



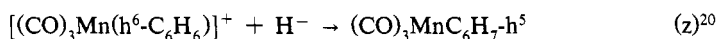
where dppe is $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$. Cleavage of the reduced product occurs in the reaction of $HMn(CO)_5$ with $PhC(Me)=CH_2$:

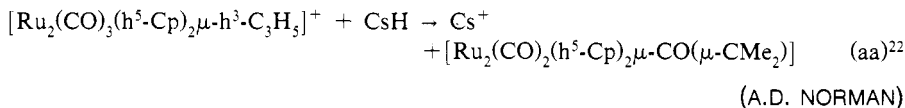


Reaction of a diene with $[HNiL_4]^+$ yields the h^3 -product:



Hydride-ion reactions with the ligands of some cationic organometallic complexes results in C—H bond formation, e.g.:

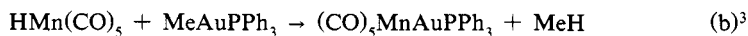
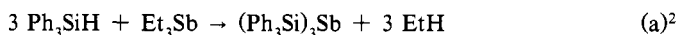




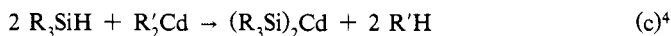
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3. M. Montury, J. Gore, *Tetrahedron Lett.*, **21**, 51 (1980).
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8. F. Glockling, *The Chemistry of Germanium*, Academic Press, London, 1969.
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13. R. Uriarte, T. J. Mazanec, K. D. Tau, D. W. Meek, *Inorg. Chem.*, **19**, 79 (1980).
14. W. R. Cullen, *Adv. Organomet. Chem.*, **4**, 145 (1966).
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16. B. N. Diel, R. C. Haltiwanger, A. D. Norman, *J. Am. Chem. Soc.*, **104**, 4700 (1982).
17. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961.
18. G. H. Whitam, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 1, J. F. Stoddart, ed., Pergamon Press, Oxford, 1979, p. 121.
19. G. P. Chiusoli, G. Salerno, *Adv. Organomet. Chem.*, **17**, 195 (1979).
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22. D. D. Davies, A. F. Dyke, A. Endesfelder, S. A. R. Knox, P. J. Naish, A. G. Oipen, D. Plass, G. E. Taylor, *J. Organomet. Chem.*, **198**, C43 (1980).

1.6.4.1.5. from Other Derivatives.

Hydride cleavage of carbon–element σ -bonds frequently results in C—H bond formation¹, although often the other cleavage product is of primary interest, e.g.:

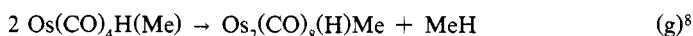
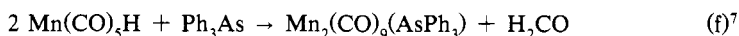
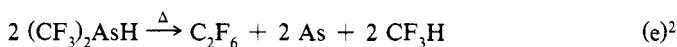


Cleavage of organic moieties from Cd, Zn, Hg or Mg in their organometallic compounds can be important in organic synthesis, e.g.:

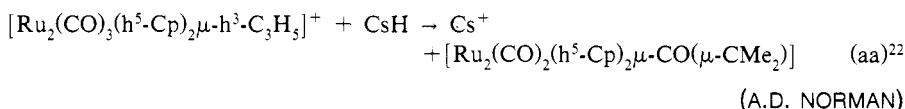


where R and R' = alkyl or aryl.

Reductive elimination (thermal or photochemical) can form C—H bonds, although it is not a preferred synthesis of C—H bond-containing products^{1–5,8,9}, e.g.:



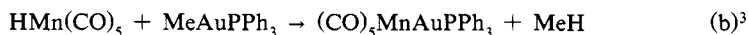
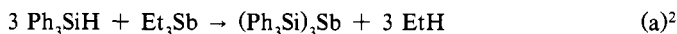
88 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.4. by Hydride Reduction
 1.6.4.1. Giving Hydrides of Carbon



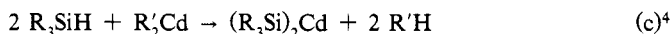
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1.6.4.1.5. from Other Derivatives.

Hydride cleavage of carbon–element σ -bonds frequently results in C—H bond formation¹, although often the other cleavage product is of primary interest, e.g.:

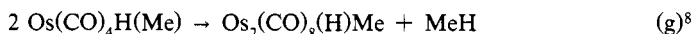
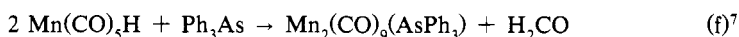
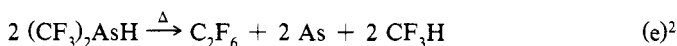


Cleavage of organic moieties from Cd, Zn, Hg or Mg in their organometallic compounds can be important in organic synthesis, e.g.:



where R and R' = alkyl or aryl.

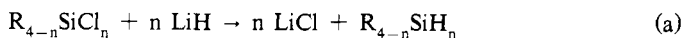
Reductive elimination (thermal or photochemical) can form C—H bonds, although it is not a preferred synthesis of C—H bond-containing products^{1–5,8,9}, e.g.:



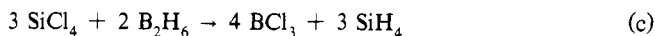
1.6.4.2. Giving Hydrides of Silicon

1.6.4.2.1. from Halides.

Alkali-metal hydrides, boranes or alanes reduce halosilanes in high yield¹⁻³:



where R = alkyl, aryl; n = 1-4;

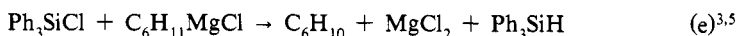


Representative reactions and products are listed in Table 1. Lithium and Na hydride reductions are performed in ether, although with $SiCl_4$ eutectic salts can be used². In large-scale syntheses NaH is prepared in situ from reaction of Na with H_2 . In the Al- $AlCl_3-H_2$ or $AlCl_3-NaCl-H_2$ reductant systems, intermediate alanes AlH_nCl_{3-n} are the active reductant.

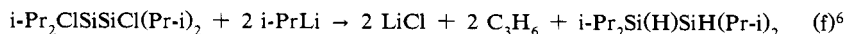
Halosilane redistributions-disproportionations produce new Si-H bonds. Fluorosilane reactions occur at 25°C, e.g.⁴:



At higher T or in the presence of $AlCl_3$ catalyst, other halosilanes react similarly^{3,4}. Reactions of halosilanes with organo-Mg:



or alkyl-Li reagents:



through reductive elimination produce silanes.

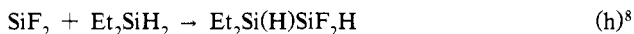
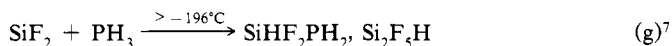
TABLE 1. HYDRIDE REDUCTION OF HALOSILANES

Halosilane	Reductant, solvent	Product	Yield (%)	Ref.
$SiCl_4$	LiH, Et_2O	SiH_4	85	1,2
$SiCl_4$	Al-NaH- H_2 $AlCl_3$ -NaCl	SiH_4	64	2
$SiCl_4$	NaH- Et_3B , THF	SiH_4	94	2
$Si(OEt)_2F_2$	NaH, C_8H_{18}	SiH_4	> 80	2,3
Si_2Cl_6	AlH_3 , Et_2O	Si_2H_6	90	2,3
$CH_2CHCH_2SiCl_3$	LiH, $(C_6H_{11})_2O$	$CH_2CHCH_2SiH_3$	85	3
$MeCHClSiCl_3$	LiH, dioxane	$MeCHClSiH_3$	^a	2,3
Me_2SiCl_2	Et_2AlH	Me_2SiH_2	100	2,3
Et_2SiF_2	NaH ^b	Et_2SiH_2	88	2,3
Et_3SiF	Et_2AlH	Et_3SiH	100	2,3
Et_3SiF	Na- H_2 ^b	Et_3SiH	90	2,3
Ph_3SiCl	NaH, C_8H_{18}	Ph_3SiH	81	2,3

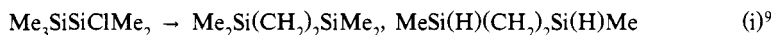
^a Not available.

^b No solvent.

Insertion of halosilenes into substrate-H bonds yields silanes:



Thermolysis of a halodisilane at 600–700°C produces insertion products containing SiH bonds:

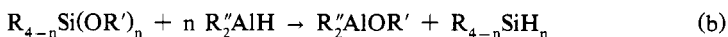
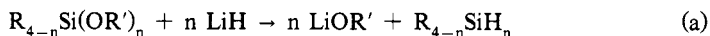


(A.D. NORMAN)

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9. P. G. Harrison, *Coord. Chem. Rev.*, **40**, 179 (1982).

1.6.4.2.2. from Oxygen Compounds.

Alkali-metal hydrides, boranes or alanes react with alkoxysilanes or silanols to form Si—H bonds in reactions that often are preferred syntheses, depending on the availability of the silane reactant^{1–4}. Lithium hydride or alaanate reductions used are:



Typical reactions and products are listed in Table 1. Reductions involving H₂ in NaCl–AlCl₃ solvents or H₂ in the presence of Na involve AlCl_{3–n}H_n or NaH, respectively, as reductant species.

TABLE 1. HYDRIDE REDUCTION OF SILICON–OXYGEN COMPOUNDS

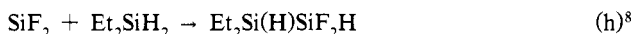
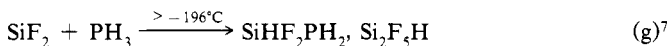
Reactant silane	Reductant, solvent	Product	Yield (%)	Ref.
NaSiO ₃	AlCl ₃ –NaCl–H ₂ , AlCl ₃ –NaCl	SiH ₄	20	1,2
Si(OEt) ₄	AlCl ₃ –NaCl–H ₂ , AlCl ₃ –NaCl	SiH ₄	16	1
(SiH ₃) ₂ O	B ₂ H ₆ ^a	SiH ₄	95	2,3
SiCl ₂ (OEt) ₂	NaH, octane	SiH ₄	80	2,4
Et ₂ Si(OEt) ₂	LiH, (C ₅ H ₁₁) ₂ O	Et ₂ SiH ₂	45	2
Me ₂ Si(OEt) ₂	Et ₂ AlH ^a	Me ₂ SiH ₂ ^b	100	2
(Me ₃ Si ₂) ₂ O	(i-C ₄ H ₉) ₂ AlH ^a	Me ₃ SiH	81	2,4

^a No solvent.

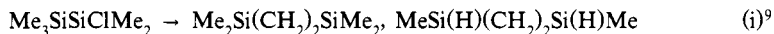
^b Some Et₂SiH₂ forms also.

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 91
 1.6.4. by Hydride Reduction
 1.6.4.2. Giving Hydrides of Silicon

Insertion of halosilenes into substrate—H bonds yields silanes:



Thermolysis of a halodisilane at 600–700°C produces insertion products containing SiH bonds:

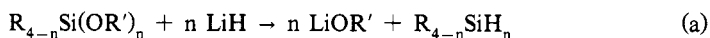


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Alkali-metal hydrides, boranes or alanes react with alkoxysilanes or silanols to form Si—H bonds in reactions that often are preferred syntheses, depending on the availability of the silane reactant^{1–4}. Lithium hydride or alanate reductions used are:



Typical reactions and products are listed in Table 1. Reductions involving H₂ in NaCl–AlCl₃ solvents or H₂ in the presence of Na involve AlCl_{3–n}H_n or NaH, respectively, as reductant species.

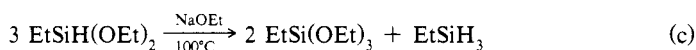
TABLE 1. HYDRIDE REDUCTION OF SILICON–OXYGEN COMPOUNDS

Reactant silane	Reductant, solvent	Product	Yield (%)	Ref.
NaSiO ₃	AlCl ₃ –NaCl–H ₂ , AlCl ₃ –NaCl	SiH ₄	20	1,2
Si(OEt) ₄	AlCl ₃ –NaCl–H ₂ , AlCl ₃ –NaCl	SiH ₄	16	1
(SiH ₃) ₂ O	B ₂ H ₆ ^a	SiH ₄	95	2,3
SiCl ₂ (OEt) ₂	NaH, octane	SiH ₄	80	2,4
Et ₂ Si(OEt) ₂	LiH, (C ₅ H ₁₁) ₂ O	Et ₂ SiH ₂	45	2
Me ₂ Si(OEt) ₂	Et ₂ AlH ^a	Me ₂ SiH ₂ ^b	100	2
(Me ₃ Si) ₂ O	(<i>i</i> -C ₄ H ₉) ₂ AlH ^a	Me ₃ SiH	81	2,4

^a No solvent.

^b Some Et₂SiH₂ forms also.

Hydridosiloxanes redistribution in the presence of catalysts yields new Si—H products⁴:



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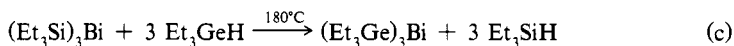
Silicon–hydrogen bonds form in reactions¹ of alkali-metal hydrides with Si_2H_6 :



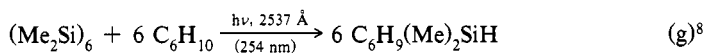
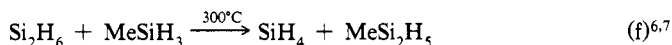
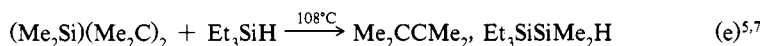
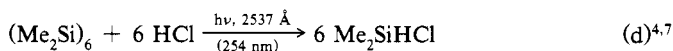
or² $\text{Ph}_3\text{SiCH}_2\text{Ph}$:



Cleavage of Si—Bi bonds by Et_3GeH produces a silane product³:



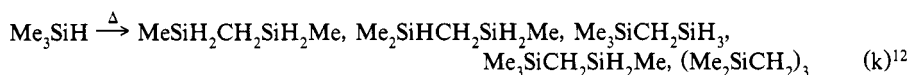
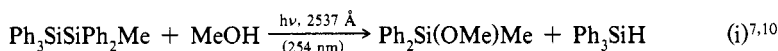
Thermolysis or photolysis of silanes produces new Si—H bonds; the reactions involve silylenes:



Through Si—Si double-bond-containing intermediates, new Si—H bonds can form:



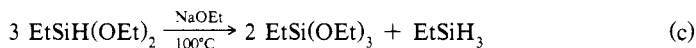
Other less well-defined thermolysis or photolysis reactions also produce silanes:



The Hg-sensitized photolysis of Si_2H_6 yields SiH_4 and higher silanes:

- 92 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.4. by Hydride Reduction
 1.6.4.2. Giving Hydrides of Silicon

Hydridosiloxanes redistribution in the presence of catalysts yields new Si—H products⁴:



(A.D. NORMAN)

1. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
2. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
3. L. H. Long, *Adv. Inorg. Chem. Radiochem.*, **16**, 201 (1974).
4. D. A. Armitage, in *Comprehensive Organometallic Chemistry*, Vol. 2, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 1.

1.6.4.2.3. from Other Derivatives.

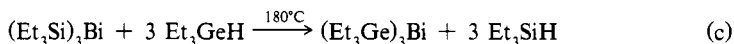
Silicon–hydrogen bonds form in reactions¹ of alkali-metal hydrides with Si_2H_6 :



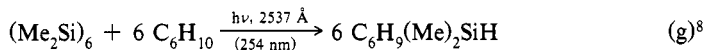
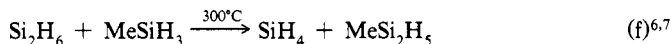
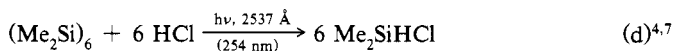
or² $\text{Ph}_3\text{SiCH}_2\text{Ph}$:



Cleavage of Si—Bi bonds by Et_3GeH produces a silane product³:



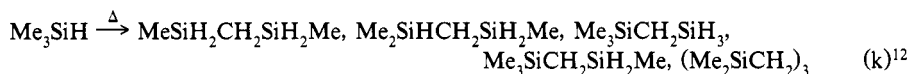
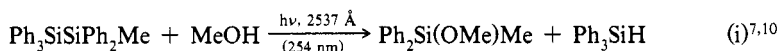
Thermolysis or photolysis of silanes produces new Si—H bonds; the reactions involve silylenes:



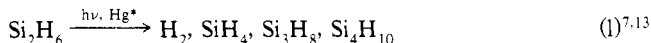
Through Si—Si double-bond-containing intermediates, new Si—H bonds can form:



Other less well-defined thermolysis or photolysis reactions also produce silanes:



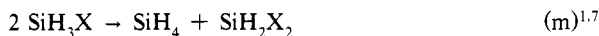
The Hg-sensitized photolysis of Si_2H_6 yields SiH_4 and higher silanes:



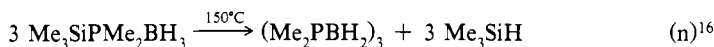
Pyrolysis of silane or silane-germane mixtures by rapid passage through a 350–370°C hot zone yields mixtures of binary and ternary silanes. Typical pyrolysis mixtures and major hydrides (in parentheses) obtained are¹⁴: SiH_4 (Si_2H_6 , Si_3H_8), Si_2H_6 (SiH_4 , Si_3H_8 , Si_4H_{10}), $\text{SiH}_4\text{--GeH}_4$ (Si_2H_6 , SiGeH_6), $\text{Ge}_2\text{H}_6\text{--Si}_2\text{H}_6$ (Si_2GeH_8) and $\text{Ge}_2\text{H}_6\text{--Si}_3\text{H}_8$ (i- and n- $\text{Si}_3\text{GeH}_{10}$).

Passage of SiH_4 , $\text{SiH}_4\text{--GeH}_4$, $\text{SiH}_4\text{--PH}_3$, or $\text{SiH}_4\text{--AsH}_3$ through a 15 kV silent electric discharge results in products, some of which involve new Si—H bond formation. Pyrolysis mixtures and major products (in parentheses) from such reactions are¹⁵: SiH_4 (Si_2H_6 , Si_3H_8), $\text{SiH}_4\text{--GeH}_4$ (Si_2H_6 , SiGeH_6 , Ge_2H_6), $\text{SiH}_4\text{--PH}_3$ [Si_2H_6 , P_2H_4 , (SiH_3) $_2\text{PH}$], $\text{Si}_2\text{H}_6\text{--PH}_3$ (SiH_4 , Si_3H_8 , $\text{Si}_2\text{H}_5\text{PH}_2$) and $\text{SiH}_4\text{--AsH}_3$ (Si_2H_6 , SiH_3AsH_2).

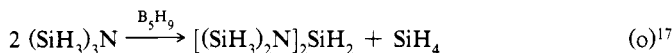
Redistribution:



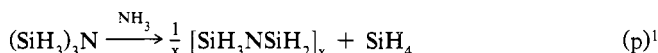
where X = halogen, alkoxy, NR_2 , or disproportionation yields new Si—H bonds^{1,7}:



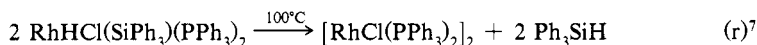
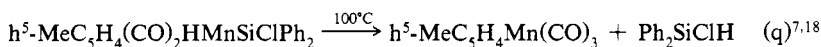
Such reactions often proceed rapidly in the liquid but only slowly in the gas phase. These reactions often can be either acid catalyzed:



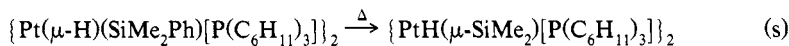
or base catalyzed:



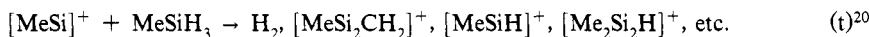
Thermal elimination of silyl and hydride moieties from silyl-metal complexes yields silanes:



Intramolecular rearrangement produces a Pt—H—Si bridge compound in low yield¹⁹:



Ion-molecule reactions in the gas phase yield new Si—H bonds in reactions that are not useful synthetically:



(A.D. NORMAN)

1. B. J. Ayelett, *Adv. Inorg. Chem. Radiochem.*, **11**, 249 (1968).
2. K. Ruhlmann, *Z. Chem.*, **6**, 421 (1966).
3. F. Glockling, *The Chemistry of Germanium*, Academic Press, London, 1969.

4. P. G. Harrison, *Coord. Chem. Rev.*, **40**, 179 (1982).
5. D. Seyferth, D. C. Annarelli, *J. Am. Chem. Soc.*, **97**, 7162 (1975).
6. M. D. Sefcik, M. A. Ring, *J. Am. Chem. Soc.*, **95**, 5168 (1973).
7. D. Armitage, in *Comprehensive Organometallic Chemistry*, Vol. 2, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 1.
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10. P. Boudjouk, J. R. Roberts, C. M. Golino, L. H. Sommer, *J. Am. Chem. Soc.*, **94**, 7926 (1972).
11. S. H. M. Ho, J. D. Halten, III, S. Konieczny, E. C-L. Ma, P. P. Gaspar, *J. Am. Chem. Soc.*, **104**, 1424 (1982).
12. G. Ritz, J. Maas, A. Hornung, *Z. Anorg. Allg. Chem.*, **460**, 115 (1980).
13. T. L. Pollack, H. S. Sandhur, A. Jodhan, O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 1017 (1973).
14. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
15. W. L. Jolly, A. D. Norman, *Prep. Inorg. React.*, **4**, 1 (1968).
16. E. W. Abel, S. M. Illingworth, *Organomet. Chem. Rev.*, **A**, **5**, 143 (1970).
17. W. M. Scantlin, A. D. Norman, *J. Chem. Soc., Chem. Commun.*, 1246 (1971).
18. U. Schubert, B. Wörle, P. Jandik, *Angew. Chem., Int. Ed. Engl.*, **20**, 695 (1981).
19. M. Auburn, M. Ciriano, J. A. K. Howard, M. Murray, N. J. Pugh, J. L. Spencer, F. G. A. Stone, P. Woodward, *J. Chem. Soc., Dalton Trans.*, 659 (1980).
20. T. M. Mayer, F. W. Lampe, *J. Phys. Chem.*, **78**, 2422 (1972).
21. M. D. Sefcik, J. M. S. Henis, P. P. Gaspar, *J. Chem. Phys.*, **61**, 4329 (1974).

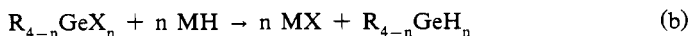
1.6.4.3. Giving Hydrides of Germanium

1.6.4.3.1. from Halides.

Alkali-metal hydrides in ether reduce¹ GeCl_4 :



or alkyl- and aryl-substituted halogermanes:



where R = alkyl, aryl; X = Cl, Br, I; M = Li, Na, K, to germanes^{2,3}. From these reactions germanes such as $\text{R}_{4-n}\text{GeH}_n$ ($n = 1-3$; R = Me, Et, i-Pr), EtMe_2GeH and Ph_3GeH are readily obtained. Yields are better using complex hydride reducing agents (see §1.6.5.3.1). In some cases, e.g., NaH reactions, reduction is catalyzed³ by the presence of electron-pair acceptor acids such as R_2AlCl .

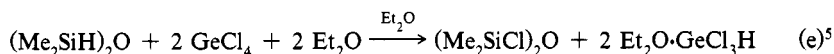
Substituted alane reduction of GeCl_4 produces⁴ GeH_4 :



Organosilane reactions with Ge tetrahalides provide near quantitative yields of trihalogermanes:



where R = Me, Et, Ph; or:



Halogermane redistribution-disproportionation forms Ge—H bonds. Fluorogermanes react at 25°C:



94 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.4. by Hydride Reduction

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or alkyl- and aryl-substituted halogermenes:



where R = alkyl, aryl; X = Cl, Br, I; M = Li, Na, K, to germanes^{2,3}. From these reactions germanes such as $\text{R}_{4-n}\text{GeH}_n$ ($n = 1-3$; R = Me, Et, i-Pr), EtMe_2GeH and Ph_3GeH are readily obtained. Yields are better using complex hydride reducing agents (see §1.6.5.3.1). In some cases, e.g., NaH reactions, reduction is catalyzed³ by the presence of electron-pair acceptor acids such as R_2AlCl .

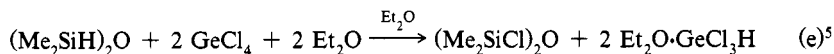
Substituted alane reduction of GeCl_4 produces⁴ GeH_4 :



Organosilane reactions with Ge tetrahalides provide near quantitative yields of trihalogermenes:



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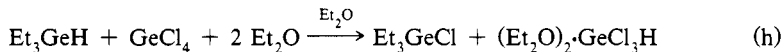
Halogermene redistribution-disproportionation forms Ge—H bonds. Fluorogermenes react at 25°C:



where R = Me, Et, n-Bu. Chlorogermane reactions occurs similarly and are catalyzed by AlCl_3 :



where R = Me, Et, Ph. However, with AlCl_3 present, Ge—C bond cleavage in arylgermanes also can occur. Triethylgermane reacts with GeCl_4 in Et_2O to form GeCl_3H in 80% yield³:



Insertion of GeF_2 into the M—H bond of trialkylsilanes, -germanes or -stannanes yields marginally stable fluorogermanes:



where M = Si, Ge, Sn; R = Et, n-Bu.

(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. M. Lesbre, D. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971.
3. P. Rivière, M. Rivière-Baudet, J. Satgé, *Comprehensive Organometallic Chemistry*, Vol. 2, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 399.
4. G. G. Devyatykh, A. D. Zorin, I. A. Frolov, R. P. Rostinova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1396 (1971).
5. V. F. Mironov, T. K. Gar, *J. Gen. Chem. USSR (Engl. Transl.)*, 45, 94 (1975).
6. P. Rivière, J. Satgé, A. Boy, *J. Organomet. Chem.*, 96, 25 (1975).

1.6.4.3.2. from Oxygen Compounds.

Germanium dioxide reacts with $(i\text{-Bu})_2\text{AlH}$ in the absence of solvent to form¹ GeH_4 :

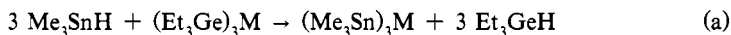


(A.D. NORMAN)

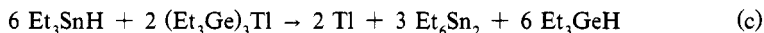
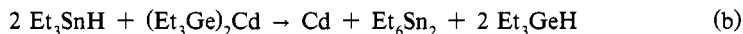
1. G. G. Devyatykh, A. D. Zorin, I. A. Frolov, R. P. Rostunova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 16, 1396 (1971).

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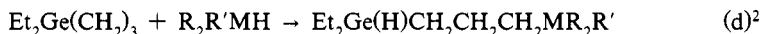
Germanium–hydrogen bonds are formed by trialkylstannane cleavage of Ge—Sb, Ge—Bi, Ge—Cd or Ge—Tl bonds^{1,2}:



where M = Sb, Bi;



Silane or germane cleavage of Ge—C bonds, in H_2PtCl_6 -catalyzed reactions e.g.:

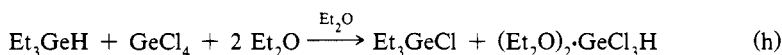


1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb	95
1.6.4. by Hydride Reduction	
1.6.4.3. Giving Hydrides of Germanium	

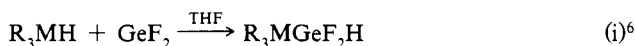
where R = Me, Et, n-Bu. Chlorogermane reactions occurs similarly and are catalyzed by AlCl_3 :



where R = Me, Et, Ph. However, with AlCl_3 present, Ge—C bond cleavage in arylgermanes also can occur. Triethylgermane reacts with GeCl_4 in Et_2O to form GeCl_3H in 80% yield³:



Insertion of GeF_2 into the M—H bond of trialkylsilanes, -germanes or -stannanes yields marginally stable fluorogermanes:



where M = Si, Ge, Sn; R = Et, n-Bu.

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Germanium dioxide reacts with $(i\text{-Bu})_2\text{AlH}$ in the absence of solvent to form¹ GeH_4 :

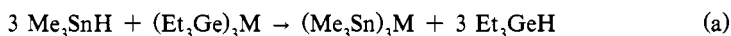


(A.D. NORMAN)

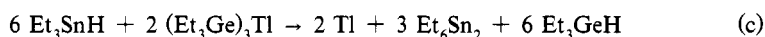
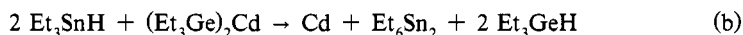
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1.6.4.3.3. from Other Derivatives.

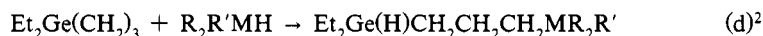
Germanium–hydrogen bonds are formed by trialkylstannane cleavage of Ge—Sb, Ge—Bi, Ge—Cd or Ge—Tl bonds^{1,2}:



where M = Sb, Bi;



Silane or germane cleavage of Ge—C bonds, in H_2PtCl_6 -catalyzed reactions e.g.:

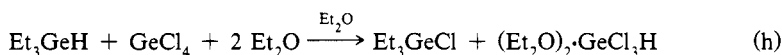


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where R = Me, Et, n-Bu. Chlorogermane reactions occurs similarly and are catalyzed by AlCl_3 :



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6. P. Rivière, J. Satgé, A. Boy, *J. Organomet. Chem.*, 96, 25 (1975).

1.6.4.3.2. from Oxygen Compounds.

Germanium dioxide reacts with $(i\text{-Bu})_2\text{AlH}$ in the absence of solvent to form¹ GeH_4 :

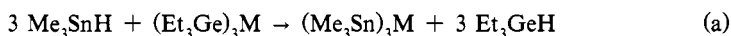


(A.D. NORMAN)

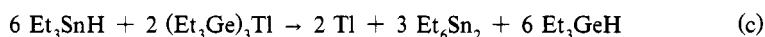
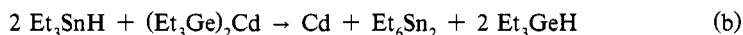
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1.6.4.3.3. from Other Derivatives.

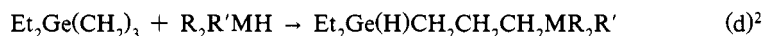
Germanium–hydrogen bonds are formed by trialkylstannane cleavage of Ge—Sb, Ge—Bi, Ge—Cd or Ge—Tl bonds^{1,2}:



where M = Sb, Bi;

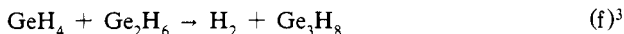


Silane or germane cleavage of Ge—C bonds, in H_2PtCl_6 -catalyzed reactions e.g.:

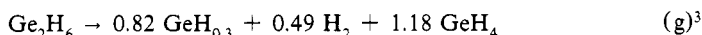


where $M = \text{Ge}$; $R = \text{Me}$, $R' = \text{Et}$; $M = \text{Si}$; $R_2R' = \text{Et}_3$, Ph_2Me , Me_2Cl , results in germabutane ring opening to the acyclic germane products.

Thermolysis of germanes yields products containing new $\text{Ge}-\text{H}$ bonds. Germane decomposes to Ge , H_2 and Ge subhydride when heated at 280°C . However, if heated at low P in a gas-circulating system, small quantities of Ge_2H_6 and Ge_3H_8 are formed³:



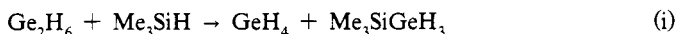
Digermane at $195\text{--}220^\circ\text{C}$ undergoes thermolysis:



If heated in the presence of trapping reagents, e.g., Me_3GeH :



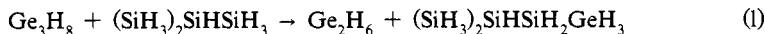
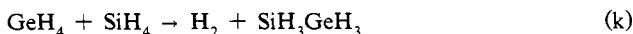
or Me_3SiH :



products result from GeH_2 insertion into $\text{Ge}-\text{H}$ or $\text{Si}-\text{H}$ bonds, respectively⁴. Similarly, $\text{Me}_3\text{Ge}_2\text{H}$ undergoes thermolysis to form a trigermane⁵:

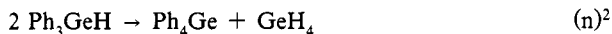


Pyrolysis of germane-silane mixtures by their rapid passage through a $350\text{--}370^\circ\text{C}$ hot zone yields mixtures of binary and ternary hydrides^{3,6}. Typical pyrolysis mixtures and the major ternary hydride products obtained are³: $\text{SiH}_4\text{--GeH}_4$, SiGeH_6 ; $\text{Ge}_2\text{H}_6\text{--Si}_2\text{H}_6$, Si_2GeH_8 ; $\text{Si}_3\text{H}_8\text{--Ge}_2\text{H}_6$, *i*- and *n*- $\text{Si}_3\text{GeH}_{10}$ and *n*- $\text{Si}_4\text{H}_{10}\text{--Ge}_3\text{H}_8$, *n*- $\text{Si}_4\text{GeH}_{12}$. Such reactions, likely involving GeH_2 intermediates, proceed:



The Hg -sensitized photolysis of GeH_4 yields⁷ some Ge_2H_6 , and the X -irradiation of $\text{Ge}_2\text{H}_6\text{--C}_2\text{H}_4$ mixtures yields⁸ EtGe_2H_5 , EtGe_3H_7 , etc., in processes that may involve formation of new $\text{Ge}-\text{H}$ bonds.

Phenylgermane at 200°C and Ph_3GeH at 300°C disproportionate:

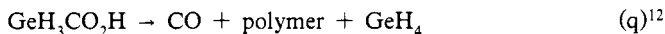
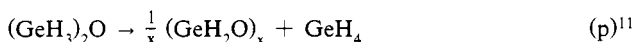


Reactions are instantaneous in the presence of AlCl_3 .

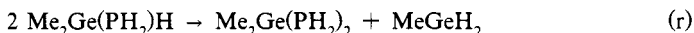
h^1 -Cyclopentadienylgermane disproportionates in the presence of Et_2NH to a mixture of Ge_2H_6 , Ge_3H_8 , C_5H_6 and solid Ge hydrides⁹.

Passage of GeH_4 , $\text{GeH}_4\text{--SiH}_4$, $\text{GeH}_4\text{--PH}_3$ or $\text{GeH}_4\text{--AsH}_3$ through a 15-kV silent electric discharge gives products, some of which are likely the result of new $\text{Ge}-\text{H}$ bond formation³, e.g., GeH_4 (Ge_2H_6 , Ge_3H_8), $\text{GeH}_4\text{--SiH}_4$ (Ge_2H_6 , Si_2H_6 and SiH_3GeH_3), $\text{GeH}_4\text{--PH}_3$ (Ge_2H_6 , P_2H_4 and GeH_3PH_2) and $\text{GeH}_4\text{--AsH}_3$ (Ge_2H_6 and GeH_3AsH_2). Lesser products form also. From the GeH_4 and $\text{GeH}_4\text{--SiH}_4$ reactions, germanes to Ge_5H_{12} and silylgermanes to $\text{SiGe}_4\text{H}_{12}$ are formed⁶.

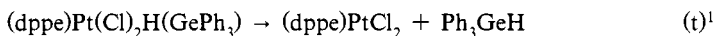
Disproportionation of GeH_3 -substituted compounds, e.g., $(\text{GeH}_3)_3\text{P}$, $(\text{GeH}_3)_2\text{O}$ and $\text{GeH}_3\text{CO}_2\text{H}$, yields GeH_4 along with higher mol wt products or uncharacterized polymers:



Similar equilibrium disproportionations of $\text{MeGe}(\text{PH}_2)_2\text{H}$ and $\text{Me}_2\text{Ge}(\text{PH}_2)\text{H}$ yields mixtures of phosphinogermanes¹³:



Thermal elimination of germyl and hydride moieties from germyl metal hydrides yields germanes:



where $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

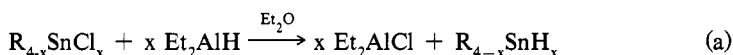
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1.6.4.4. Giving Hydrides of Tin

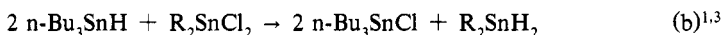
1.6.4.4.1. from Halides.

Reductions of chlorostannanes by substituted alanes constitute excellent syntheses of stannanes^{1,2}, e.g.:



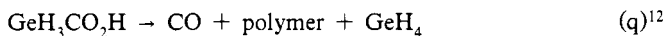
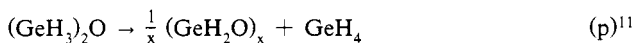
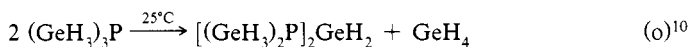
where $\text{R} = \text{Me}, \text{Et}, n\text{-Bu}, \text{Ph}$; $x = 1-3$. Representative hydrides formed and % yields are²: EtSnH_3 , 97; $n\text{-BuSnH}_3$, 62; PhSnH_3 , 72; Et_2SnH_2 , 84; $i\text{-Bu}_2\text{SnH}_2$, 72 and Et_3SnH , 89.

Diorganostannanes are prepared by exchange reactions, e.g., $n\text{-Bu}_3\text{SnH}$ with organodihalostannanes:

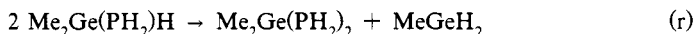


where $\text{R} = \text{Me}, \text{Et}, \text{Ph}$. Exchange is useful for the synthesis of halohydrides because the equilibria involved often favor the mixed-substituent products⁴:

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 97
 1.6.4. by Hydride Reduction



Similar equilibrium disproportionations of $\text{MeGe}(\text{PH}_2)_2\text{H}$ and $\text{Me}_2\text{Ge}(\text{PH}_2)\text{H}$ yields mixtures of phosphinogermanes¹³:



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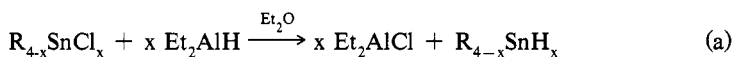
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1.6.4.4. Giving Hydrides of Tin

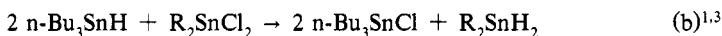
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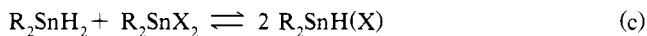


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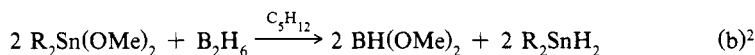
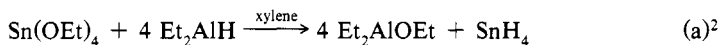
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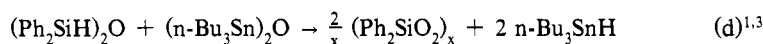
1.6.4.4.2. from Oxygen Compounds.

Substituted alanes or B_2H_6 react with alkoxystannanes forming stannanes^{1,2} in high yields:

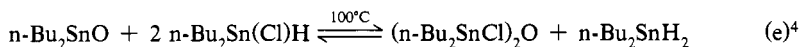


where R = Me, Et, n-C₃H₇, Ph. Typical products and % yields are^{1,2}: SnH₄, 32; Et₂SnH₂, 91; n-Bu₃SnH, 100 and Ph₃SnH, 76.

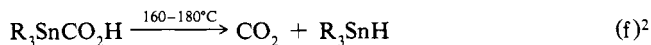
Reduction of organostannyl oxides or alkoxides is effected with hydridosiloxanes, such as (MeSiHO)_n or (Ph₂SiH)₂O:



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Trialkylformylstannanes upon thermolysis eliminate CO₂:



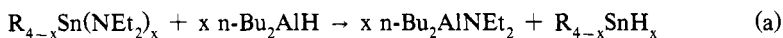
where R = i-Pr, n-Bu.

(A.D. NORMAN)

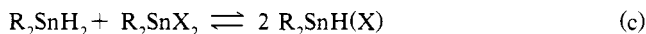
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1.6.4.4.3. from Other Derivatives.

N-Diethylaminostannanes are converted¹ to stannanes in yields up to 99% by n-Bu₂AlH or B₂H₆.



- 98 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.4. by Hydride Reduction
 1.6.4.4. Giving Hydrides of Tin



where R = Et, n-Bu, Ph; X = F, Cl, Br.

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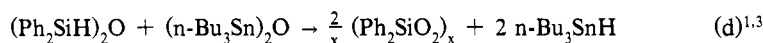
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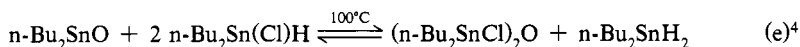


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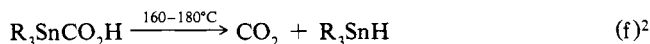
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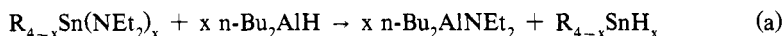
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(A.D. NORMAN)

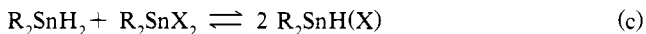
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- 98 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.4. by Hydride Reduction
 1.6.4.4. Giving Hydrides of Tin



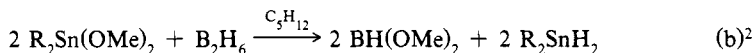
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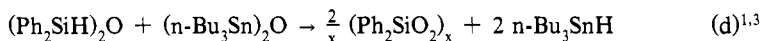
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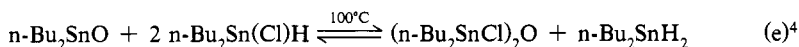


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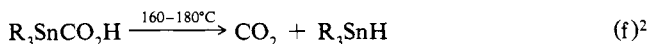
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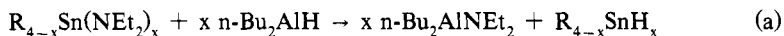
where R = i-Pr, n-Bu.

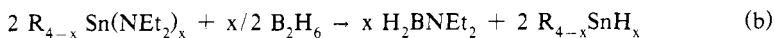
(A.D. NORMAN)

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1.6.4.4.3. from Other Derivatives.

N-Diethylaminostannanes are converted¹ to stannanes in yields up to 99% by n-Bu₂AlH or B₂H₆.





where R = Me, Et, n-Bu, Ph; x = 1–3.

Dialkyl- or diarylstannanes react with formamidostannanes to form distannanes:



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

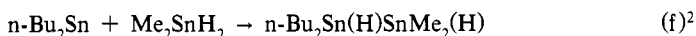
Exchange occurs between organostannanes and $(R_3Sn)_2Hg$ compounds:



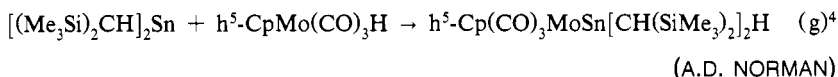
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Dialkylstannylenes insert into Sn—H bonds forming new Sn—H bond-containing products:



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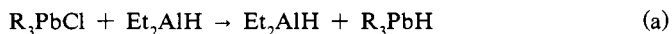


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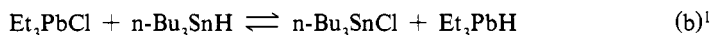
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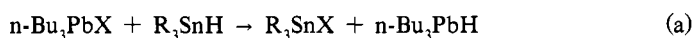


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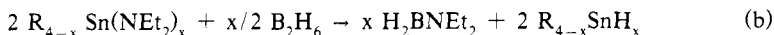
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1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 99
 1.6.4. by Hydride Reduction



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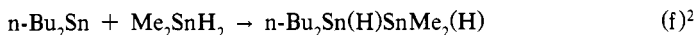
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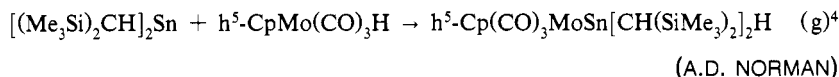
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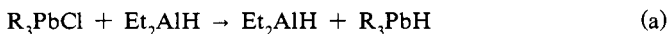


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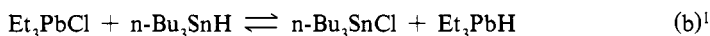
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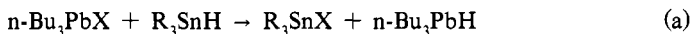


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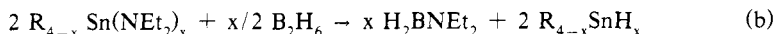
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1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 99
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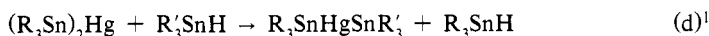
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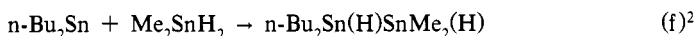
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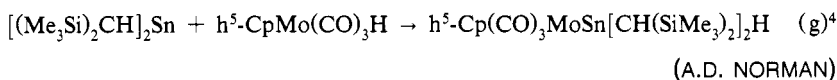
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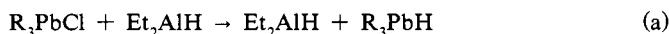


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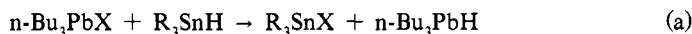


(A.D. NORMAN)

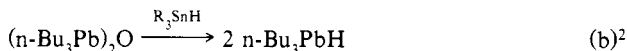
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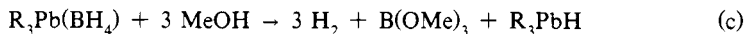
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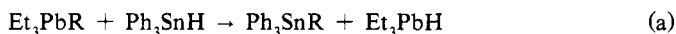
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(A.D. NORMAN)

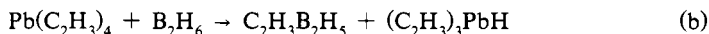
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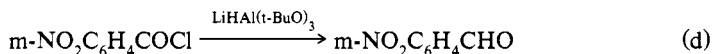
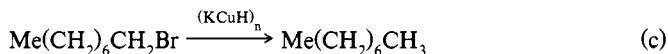
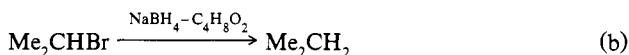
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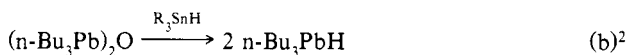
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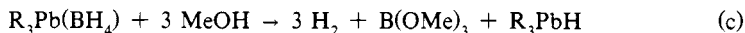


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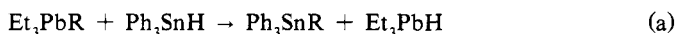
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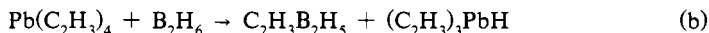
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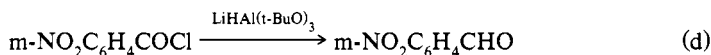
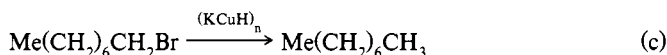
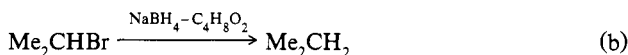
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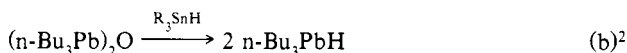
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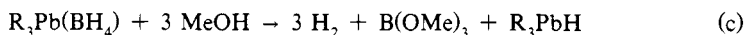


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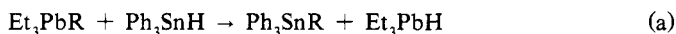
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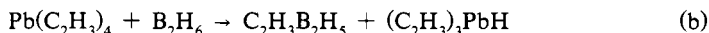
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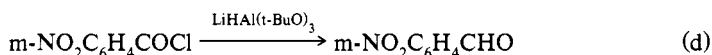
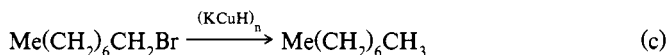
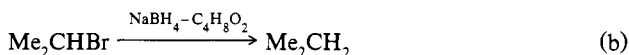
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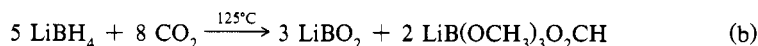
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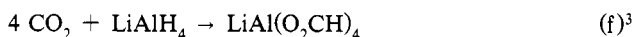
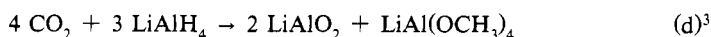
Lithium tetrahydroborate and CO₂ react at 25°C and 125°C^{1,2}, respectively:



In contrast, NaBH₄ and CO₂ at 25°C yield only the formatehydroborate ion²:



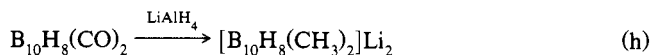
Reduction of CO₂ with 3, 2, or 1 equiv of LiAlH₄ occurs:



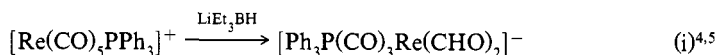
Carbon monoxide in MeOH reacts with LiAlH₄:



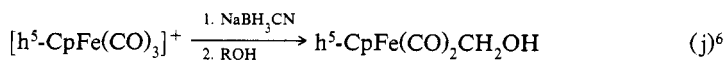
Borane carbonyls, e.g., B₁₀H₈(CO)₂, are reduced¹ by LiAlH₄:



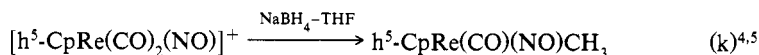
Metal-coordinated carbonyl moieties are reduced by hydroborates or hydroaluminates to formyl:



alcohol:



or alkyl derivatives in high yields^{4,5}:



1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb	101
1.6.5. by Complex Hydride Reduction	
1.6.5.1. Giving Hydrides of Carbon	

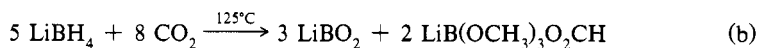
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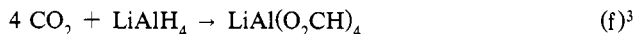
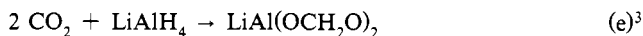
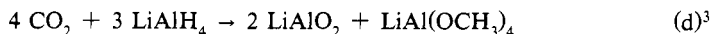
Lithium tetrahydroborate and CO₂ react at 25°C and 125°C^{1,2}, respectively:



In contrast, NaBH₄ and CO₂ at 25°C yield only the formatohydroborate ion²:



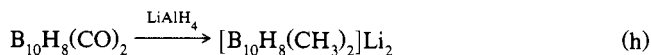
Reduction of CO₂ with 3, 2, or 1 equiv of LiAlH₄ occurs:



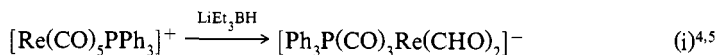
Carbon monoxide in MeOH reacts with LiAlH₄:



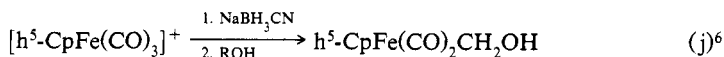
Borane carbonyls, e.g., B₁₀H₈(CO)₂, are reduced¹ by LiAlH₄:



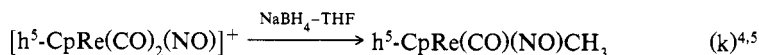
Metal-coordinated carbonyl moieties are reduced by hydroborates or hydroaluminates to formyl:



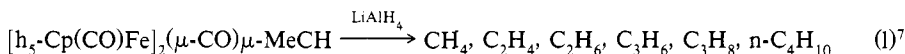
alcohol:



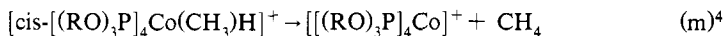
or alkyl derivatives in high yields^{4,5}:



Reduction of a diiron complex by LiAlH_4 yields hydrocarbons:



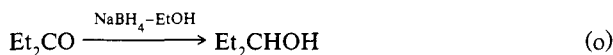
Intramolecular reductive elimination from $[(\text{RO})_3\text{P}]_4\text{Co}(\text{CH}_3)\text{H}]^+$ yields CH_4 :



Organic oxygen compounds, e.g., aldehydes:



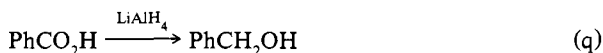
ketones:



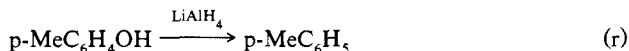
acid chlorides:



carboxylic acids:



and alcohols:



are reduced by complex hydrides^{1-3,8,9}. Some reactions occur directly to final reduced products:



However, most are two step, reduction followed by hydrolysis.

(A.D. NORMAN)

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7. S. C. Kao, P. P. Y. Liu, R. Pettit, *Organometallics*, **1**, 911 (1982).
8. H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972.
9. C. A. Buehler, D. E. Pearson, *Survey of Organic Syntheses*, Vol. 2, Wiley-Interscience, New York, 1977.

1.6.5.1.3. from Nitrogen Compounds.

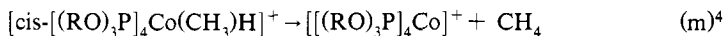
Complex metal hydroborates and hydroaluminates, hydridoferrates and modified complex hydrides (e.g., $\text{NaBH}_4\text{-AlCl}_3$) reduce organic N-containing compounds¹⁻⁴ (see also §1.5.5.1), e.g., amides:

102 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.5. by Complex Hydride Reduction
 1.6.5.1. Giving Hydrides of Carbon

Reduction of a diiron complex by LiAlH_4 yields hydrocarbons:



Intramolecular reductive elimination from $[(\text{RO})_3\text{P}]_4\text{Co}(\text{CH}_3)_3\text{H}^+$ yields CH_4 :



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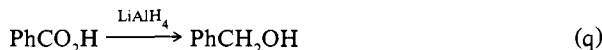
ketones:



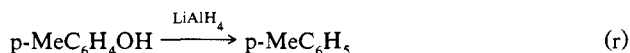
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and alcohols:



are reduced by complex hydrides^{1-3,8,9}. Some reactions occur directly to final reduced products:



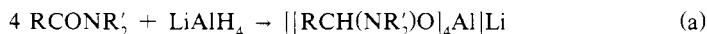
However, most are two step, reduction followed by hydrolysis.

(A.D. NORMAN)

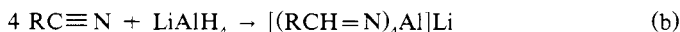
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and nitriles:



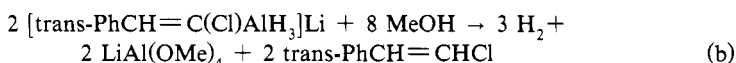
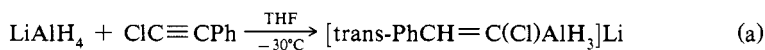
Hydrolysis yields final reduction products¹⁻³. Reaction mixtures containing Mo salts and sulfur ligands, in aqueous base, with NaBH_4 as the reducing agent, when treated with nitriles, isonitriles or $[\text{CN}]^-$ react to produce hydrocarbons (CH_4 , C_2H_2 , etc.) in reactions of undetermined stoichiometry⁵.

(A.D. NORMAN)

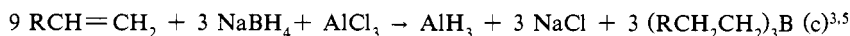
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1.6.5.1.4. from Compounds with Carbon-Carbon Multiple Bonds.

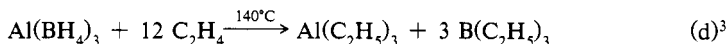
Alkenes and alkynes react with complex hydrides only under special conditions¹. Reaction products are often intermediates prior to solvolysis to the final hydrocarbons desired in organic syntheses¹⁻⁵, e.g.:



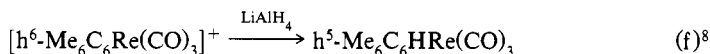
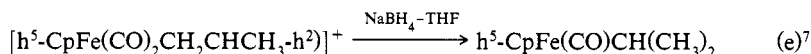
Such reactions, especially those of MBH_4 ($\text{M} = \text{Li, Na}$), occur most easily in the presence of acids (e.g., AlCl_3 or $\text{BF}_3\cdot\text{OEt}_2$) as catalysts:



Aluminum tetrahydroborate reacts with alkenes or alkynes:



Metal tetrahydroborates and tetrahydroaluminates can react with coordinated unsaturated organic molecules without ligand displacement:

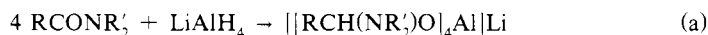


In other cases, reduction accompanied by cleavage of the organic moiety from the metal occurs.

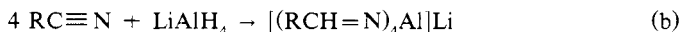


(A.D. NORMAN)

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb	103
1.6.5. by Complex Hydride Reduction	
1.6.5.1. Giving Hydrides of Carbon	



and nitriles:



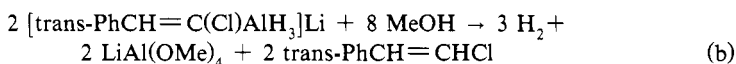
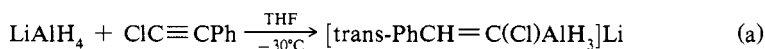
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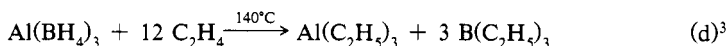
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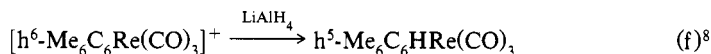
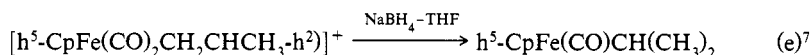
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Aluminum tetrahydroborate reacts with alkenes or alkynes:



Metal tetrahydroborates and tetrahydroaluminates can react with coordinated unsaturated organic molecules without ligand displacement:



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1.6.5.2. Giving Hydrides of Silicon

1.6.5.2.1. from Halides.

Silicon halides react with complex hydrides to form silanes. Complex hydrides used are LiAlH_4 and to a lesser extent MBH_4 ($\text{M} = \text{Li, Na, K}$)^{1,2}. Reductions are carried out in aprotic ether solvents, e.g., Et_2O , glymes, THF or $n\text{-Bu}_2\text{O}$. These reactions are adaptable to Si—D bond synthesis (see §1.6.7.1.2). Typical syntheses of monosilanes are shown in Table 1. Chlorosilanes are preferred; the fluorides react less readily. Bromo- and iodosilanes react easily but offer no advantage over the more available chlorides¹.

Reduction of halosilanes by LiAlH_4 occurs:



where $\text{R} = \text{H, alkyl, aryl}$; $\text{X} = \text{F, Cl, Br}$; $n = 1\text{--}4$. Yields are high ($> 50\%$), and consequently this method is the preferred synthesis for substituted silanes.

Reduction of Si—Cl bonds in polysilanes is without extensive Si—Si bond cleavage. Reduction of $\text{Si}_n\text{Cl}_{2n+2}$ ($n = 2\text{--}5$) halides occurs, although $\text{Si}_5\text{Cl}_{12}$ reduction even at -100°C is accompanied by some bond cleavage^{1,6}. High yields of cyclosilanes ($n = 5$)⁷:

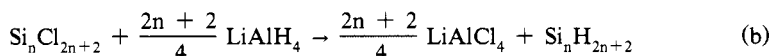


TABLE 1. COMPLEX HYDRIDE REDUCTIONS OF HALOSILANES

Reactant	Complex hydride, solvent	Product	Yield (%)	Ref.
SiCl_4	LiAlH_4 , Et_2O	SiH_4	99	1–3
SiHCl_3	NaAlH_4 , diglyme	SiH_4	100	1
Si_2Cl_6	LiAlH_4 , $n\text{-Bu}_2\text{O}$	Si_2H_6	80	1,3,4
MeSiCl_3	LiAlH_4 , dioxane	MeSiH_3	90	1,2
EtSiCl_3	LiAlH_4 , dioxane	EtSiH_3	90	1,2
PhSiCl_3	LiAlH_4 , Et_2O	PhSiH_3	70	1,2,5
Me_2SiCl_2	LiAlH_4 , dioxane	Me_2SiH_2	90	1,2
Ph_2SiCl_2	LiAlH_4 , THF	Ph_2SiH_2	76	1,2
Et_3SiCl	LiAlH_4 , dioxane	Et_3SiH	90	1,2
$(p\text{-ClC}_6\text{H}_4)_2\text{SiCl}_2$	LiAlH_4 , Et_2O	$(p\text{-ClC}_6\text{H}_4)_2\text{SiH}_2$	83	1,5

104 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.5. by Complex Hydride Reduction

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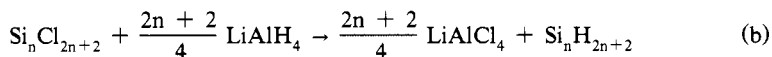
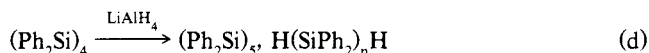


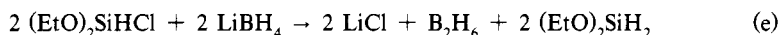
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PhSiCl_3	LiAlH_4 , Et_2O	PhSiH_3	70	1,2,5
Me_2SiCl_2	LiAlH_4 , dioxane	Me_2SiH_2	90	1,2
Ph_2SiCl_2	LiAlH_4 , THF	Ph_2SiH_2	76	1,2
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$(p\text{-ClC}_6\text{H}_4)_2\text{SiCl}_2$	LiAlH_4 , Et_2O	$(p\text{-ClC}_6\text{H}_4)_2\text{SiH}_2$	83	1,5

and oligomeric silanes ($n = 1-5$)⁸ are obtained in LiAlH_4 reductions:



Tetrahydroborates also reduce halosilanes to the parent silanes. Lithium tetrahydroborate reduces SiCl_4 to SiH_4 in high yield; in addition, it is more selective than LiAlH_4 . Lithium tetrahydroborate reacts with alkoxychlorosilanes to reduce Si—Cl bonds but without reduction of Si—O bonds, providing a good route to alkoxy silanes⁹:



Alkylchlorosilanes react with $\text{Al}(\text{BH}_4)_3$ forming alkylsilanes, e.g.:



However, reaction with SiCl_4 does not easily produce⁹ SiH_4 .

(A.D. NORMAN)

1. E. Wiberg, E. Amberger *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. D. A. Armitage, *Comprehensive Organometallic Chemistry*, Vol. 2, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 1.
3. A. D. Norman, J. R. Webster, W. L. Jolly, *Inorg. Synth.*, 11, 170 (1968).
4. M. Kumada, K. Tamao, *Adv. Organomet. Chem.*, 6, 19 (1968).
5. L. G. L. Ward, *Inorg. Synth.*, 11, 159 (1968).
6. F. Höfler, R. Jannach, *Inorg. Nucl. Chem. Lett.*, 9, 723 (1973).
7. E. Hengge, G. Bauer, *Angew. Chem., Int. Ed. Engl.*, 12, 316 (1973).
8. H. Gilman, W. H. Atwell, F. K. Cartledge, *Adv. Organomet. Chem.*, 4, 1 (1966).
9. B. D. James, M. G. H. Wallbridge, *Prog. Inorg. Chem.*, 11, 99 (1970).

1.6.5.2.2. from Oxygen Compounds.

Tetrahydroaluminate reduction of siloxanes or alkoxy silanes is an effective route to SiH_4 or alkyl or arylsilanes in ethers (Table 1)^{1,2}:

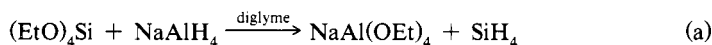


TABLE 1. COMPLEX HYDRIDE REDUCTION OF SILOXANES

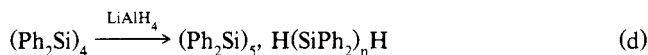
Reactant	Complex hydride, solvent	Product	Yield (%)	Ref.
$(\text{EtO})_4\text{Si}$	NaAlH_4 , diglyme	SiH_4	100	1,2
$(\text{SiCl}_2)_2\text{O}$	LiAlH_4 , Et_2O	SiH_4	100	1
$\text{SiHCl}(\text{OMe})_2$	LiBH_4^a	$(\text{MeO})_2\text{SiH}_2$	63	1,3
EtOSiHCl_2	LiBH_4^a	EtOSiH_3	40	1,3
$\text{Me}_2\text{Si}(\text{OEt})_2$	LiAlH_4 , Et_2O	Me_2SiH_2	100	1,3
$(\text{Ph}_2\text{SiH})_2\text{O}$	LiAlH_4 , Et_2O	Ph_2SiH_2	59	1
$i\text{-Pr}_3\text{SiOEt}$	LiAlH_4 , $n\text{-Bu}_2\text{O}$	$i\text{-Pr}_2\text{SiH}$	^b	1

^a No solvent.

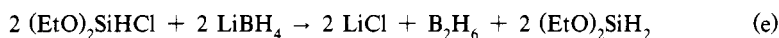
^b Not reported.

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 105
 1.6.5. by Complex Hydride Reduction
 1.6.5.2. Giving Hydrides of Silicon

and oligomeric silanes ($n = 1-5$)⁸ are obtained in LiAlH_4 reductions:



Tetrahydroborates also reduce halosilanes to the parent silanes. Lithium tetrahydroborate reduces SiCl_4 to SiH_4 in high yield; in addition, it is more selective than LiAlH_4 . Lithium tetrahydroborate reacts with alkoxychlorosilanes to reduce $\text{Si}-\text{Cl}$ bonds but without reduction of $\text{Si}-\text{O}$ bonds, providing a good route to alkoxyasilanes⁹:



Alkylchlorosilanes react with $\text{Al}(\text{BH}_4)_3$ forming alkylsilanes, e.g.:



However, reaction with SiCl_4 does not easily produce⁹ SiH_4 .

(A.D. NORMAN)

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5. L. G. L. Ward, *Inorg. Synth.*, **11**, 159 (1968).
6. F. Höfler, R. Jannach, *Inorg. Nucl. Chem. Lett.*, **9**, 723 (1973).
7. E. Hengge, G. Bauer, *Angew. Chem., Int. Ed. Engl.*, **12**, 316 (1973).
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9. B. D. James, M. G. H. Wallbridge, *Prog. Inorg. Chem.*, **11**, 99 (1970).

1.6.5.2.2. from Oxygen Compounds.

Tetrahydroaluminate reduction of siloxanes or alkoxyasilanes is an effective route to SiH_4 or alkyl or arylsilanes in ethers (Table 1)^{1,2}:

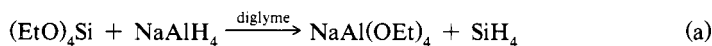


TABLE 1. COMPLEX HYDRIDE REDUCTION OF SILOXANES

Reactant	Complex hydride, solvent	Product	Yield (%)	Ref.
$(\text{EtO})_4\text{Si}$	NaAlH_4 , diglyme	SiH_4	100	1,2
$(\text{SiCl}_3)_2\text{O}$	LiAlH_4 , Et_2O	SiH_4	100	1
$\text{SiHCl}(\text{OMe})_2$	LiBH_4^a	$(\text{MeO})_2\text{SiH}_2$	63	1,3
EtOSiHCl_2	LiBH_4^a	EtOSiH_3	40	1,3
$\text{Me}_2\text{Si}(\text{OEt})_2$	LiAlH_4 , Et_2O	Me_2SiH_2	100	1,3
$(\text{Ph}_2\text{SiH})_2\text{O}$	LiAlH_4 , Et_2O	Ph_2SiH_2	59	1
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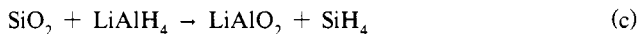
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In contrast, LiBH_4 does not reduce Si—O bonds, making it useful for selective reduction of alkoxychlorosilanes.

Silica and silica gel react with LiAlH_4 in the solid to form SiH_4 in low yields¹:



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Reaction of $\text{Al}(\text{BH}_4)_3$ with $(\text{EtO})_4\text{Si}$ yields SiH_4 nearly quantitatively:

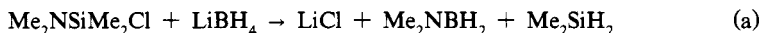


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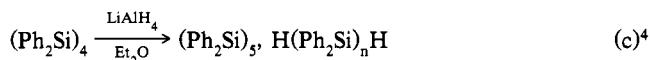
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1.6.5.3. Giving Hydrides of Germanium

1.6.5.3.1. from Halides.

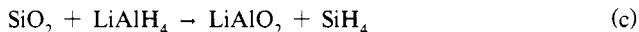
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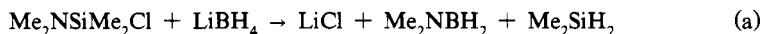


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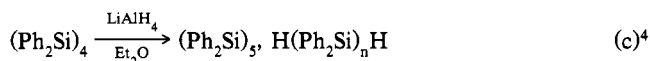
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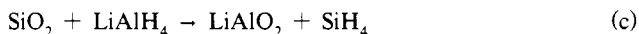
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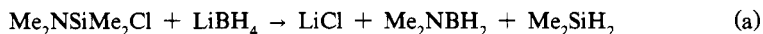


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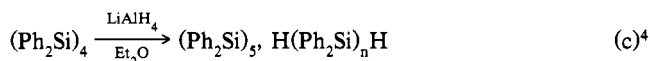
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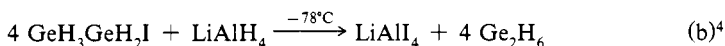
tetrahydroborate reductions can be carried out in H_2O . The hydroborate or hydroaluminate reductions are adaptable to $\text{Ge}-\text{D}$ synthesis (see §1.6.7.1.3).

Reduction of halogermanes by LiAlH_4 occurs (Table 1):

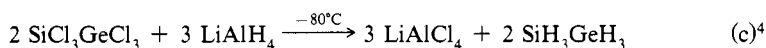


where $n = 1-4$; $\text{R} = \text{H}$, alkyl, aryl; $\text{X} = \text{Cl}$, Br , I . Yields are high. Reduction of ring compounds, e.g., diiodogermacyclopentane, occurs without $\text{Ge}-\text{C}$ bond cleavage³.

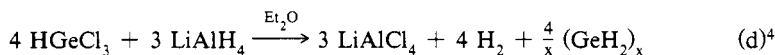
Unsubstituted halogermanes, e.g., $\text{GeH}_3\text{GeH}_2\text{I}$:



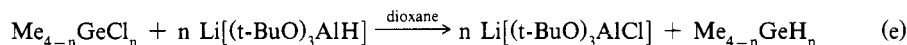
and $\text{GeCl}_3\text{SiCl}_3$:



are reduced at low T. Reactions of LiAlH_4 with GeCl_3H in Et_2O yields $(\text{GeH}_2)_x$:



Halogermane reduction by $\text{Li}[(\text{t-BuO})_3\text{AlH}]$ or $\text{Li}[\text{As}(\text{Me})_3\text{AlH}]$ yields germanes, the former reagent forming $\text{Me}_{4-n}\text{GeH}_n$ ($n = 1-4$) in yields up to 70% from the respective chlorides³:

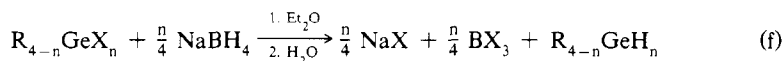


Reduction of a halogermane by its addition to a basic aq NaBH_4 or KBH_4 or to MBH_4 ($\text{M} = \text{Li}$, Na , K) in ether, followed by hydrolysis in neutral or acid H_2O , germanes in high yields of (Table 1). Germylboronate intermediate species are hydrolyzed in the last step¹⁻³.

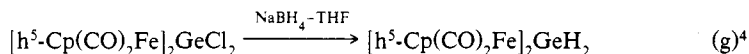
TABLE 1. COMPLEX HYDRIDE REDUCTIONS OF HALOGERMANES

Reactant	Complex hydride, solvent	Product	Yield (%)	Ref.
GeCl_4	NaBH_4 , THF^a	GeH_4	40	2,4
MeGeBr_3	NaBH_4 , $\text{HBr}_{(\text{aq})}$	MeGeH_3	99	2,3
EtGeCl_3	LiAlH_4 , Et_2O	EtGeH_3	80	3,4
$n\text{-C}_5\text{H}_{11}\text{GeBr}_3$	LiAlH_4 , $n\text{-Bu}_2\text{O}$	$n\text{-C}_5\text{H}_{11}\text{GeH}_3$	90-100	3,4
Me_2GeCl_2	LiAlH_4 , $n\text{-Bu}_2\text{O}$	Me_2GeH_2	95	6
Et_2GeCl_2	LiAlH_4 , Et_2O	Et_2GeH_2	90-100	3,4
Ph_2GeBr_2	LiAlH_4 , Et_2O	Ph_2GeH_2	67	3,4
Me_3GeBr	NaBH_4 , H_2O	Me_3GeH	95	2,3
Et_3GeCl	LiAlH_4 , Et_2O	Et_3GeH	90-100	3,4
Ph_3GeBr	LiAlH_4 , Et_2O	Ph_3GeH	60	3,4
$(i\text{-Pr}_2\text{GeCl})_2$	LiAlH_4 , Et_2O	$(i\text{-Pr}_2\text{GeH})_2$	50	7

^a Water added after reaction to hydrolyze the germylboronate.



An Fe-Ge dichloride complex is reduced with $NaBH_4$:

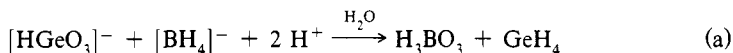


(A.D. NORMAN)

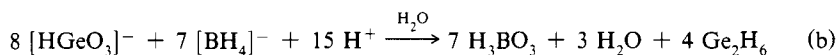
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1.6.5.3.2. from Oxygen Compounds.

Potassium or Na tetrahydroborate reduction of aqueous germanate, accomplished by adding a basic $Na_2GeO_3-KBH_4$ soln dropwise to $MeCO_2H$ or H_2SO_4 , produces GeH_4 in up to 73% yield¹:

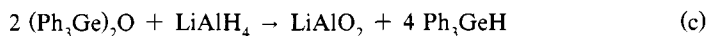


Small quantities of Ge_2H_6 :

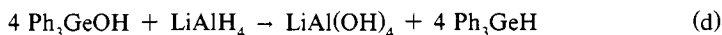


Ge_3H_8 and $(GeH_2)_x$ form also. Germanium dioxide, when heated with a deficit of powdered $LiAlH_4$ at 148–170°C, produces GeH_4 , Ge_2H_6 and Ge_3H_8 in 4, 3 and 1% yield, respectively².

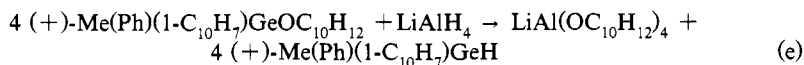
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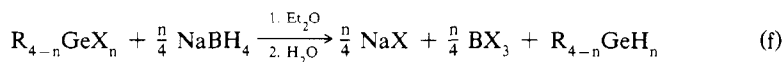


Chiral alkoxydes are reduced with retention of configuration; reduction of chiral halogermanes results in inversion of configuration⁴.

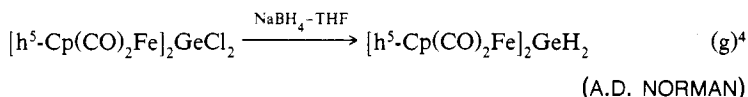
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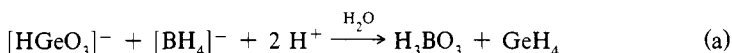
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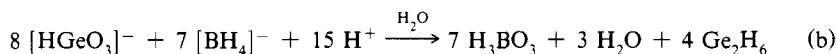
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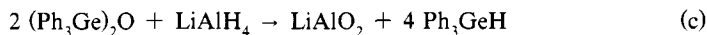


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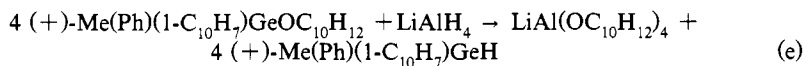
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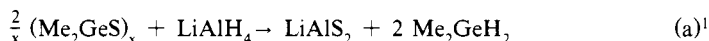
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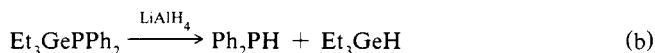
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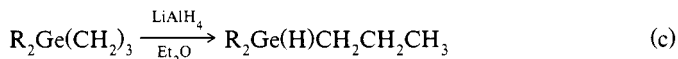
Lithium tetrahydroaluminate reduction of $(\text{Me}_2\text{GeS})_x$ occurs:



Cleavage of Ge—P bonds in acyclic² and cyclic³ germyl phosphines yields Ge—H-containing products, e.g.:



Dialkylgermacyclobutanes are cleaved⁴ slowly by LiAlH_4 in refluxing Et_2O :



Reaction of $(n\text{-Pr}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ with LiAlH_4 yields Ph_3GeH and uncharacterized Pt-containing products⁴.

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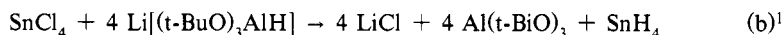
1.6.5.4. Giving Hydrides of Tin

1.6.5.4.1. from Halides.

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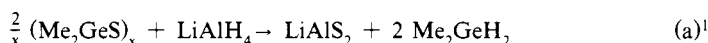
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1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 109
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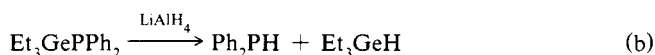
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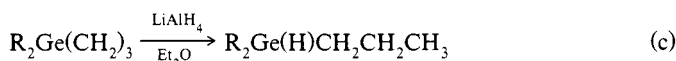
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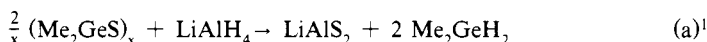
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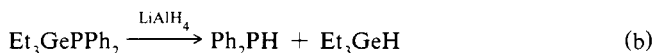
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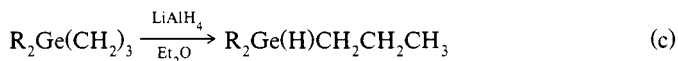
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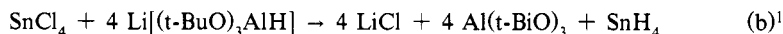
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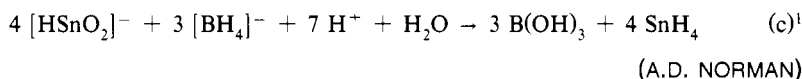


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TABLE 1. COMPLEX HYDRIDE REDUCTIONS OF HALOSTANNANES

Reactant	Complex hydride, solvent	Product	Yield (%)	Ref.
SnCl ₄	LiAlH ₄ , Et ₂ O	SnH ₄	30	1,3
MeSnCl ₃	LiAlH ₄ , Et ₂ O	MeSnH ₃	5	1,2
n-BuSnCl ₃	NaBH ₄ , monoglyme	n-BuSnH ₃	16	1,2
Me ₂ SnCl ₂	LiAlH ₄ , C ₄ H ₈ O ₂	Me ₂ SnH ₂	72	1,2
Et ₂ SnCl ₂	LiAlH ₄ , Et ₂ O	Et ₂ SnH ₂	90	1,2
Ph ₂ SnCl ₂	LiAlH ₄ , Et ₂ O	Ph ₂ SnH ₂	72	1,2
Me ₃ SnBr	LiAlH ₄ , C ₄ H ₈ O ₂	Me ₃ SnH	40	1,2
n-Pr ₃ SnCl	LiAlH ₄ , Et ₂ O	n-Pr ₃ SnH	75	1,2
n-Bu ₃ SnCl	NaBH ₄ , monoglyme	n-Bu ₃ SnH	62	4
Ph ₃ SnCl	NaBH ₄ , monoglyme	Ph ₃ SnH	82	4
(n-Bu ₂ SnCl) ₂	LiAlH ₄ , Et ₂ O	(n-Bu ₂ SnH) ₂	76	1

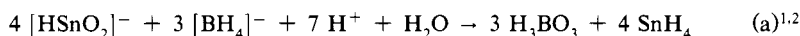
[HSnO₂]⁻, using xs NaBH₄, SnH₄ forms in 84% yield:



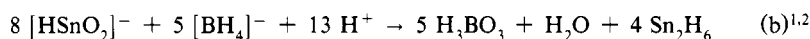
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1.6.5.4.2. from Oxygen Compounds.

Sodium tetrahydroborate reduction of stannites in H₂O produces SnH₄:

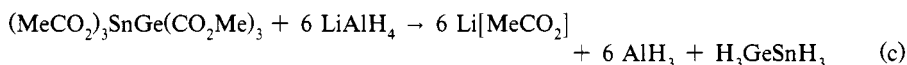


and Sn₂H₆:



Phenylstannane and MeSnH₃ form readily from NaBH₄ reduction in H₂O of PhSnCl₃ or K[MeSnO₂], respectively³.

Lithium tetrahydroaluminate reduction of acetoxystannanes e.g.:



yields Sn-H bonds effectively¹. Alkoxy-stannanes are reduced to the corresponding organostannanes⁴:



where x = 1-3; R = aryl, alkyl; R' = alkyl.

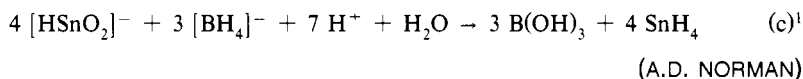
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Et ₂ SnCl ₂	LiAlH ₄ , Et ₂ O	Et ₂ SnH ₂	90	1,2
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Me ₃ SnBr	LiAlH ₄ , C ₄ H ₉ O ₂	Me ₃ SnH	40	1,2
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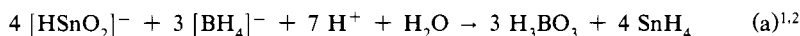
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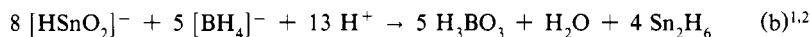
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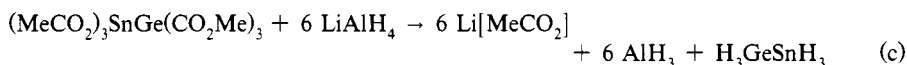


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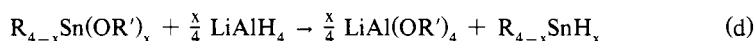


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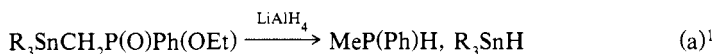
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The Sn—C bond in stannylmethylphosphonate is cleaved by LiAlH_4 :



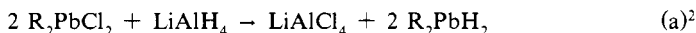
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where R = Me, Et, i-Pr, n-Bu, C_6H_{11} .

Potassium tetrahydroborate reduces⁴ trialkylhaloplumbanes in liq NH_3 :



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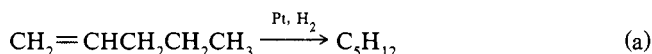
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1.6.6. by Industrial Processes

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Reactions of H_2 or H_2 sources (e.g., Zn-HCl) with alkenes, alkynes, arenes, ketones, nitriles, carboxylic acids and esters are used industrially for C—H bond formation¹⁻⁸. Heterogeneous reaction catalysts (e.g., Ni, Pt, Pd, Fe, Ni—Cu) are used, e.g.:

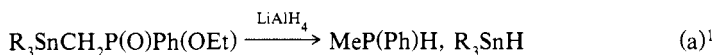


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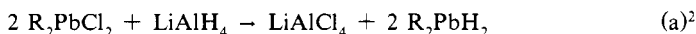
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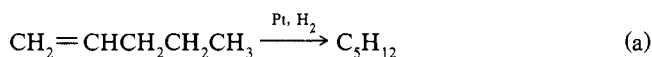
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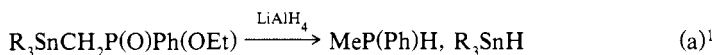


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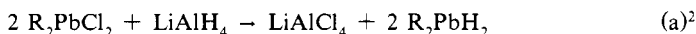
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Plumbane, because of its low thermal stability, is not isolated from reactions of complex hydride with Pb halides¹. Alkylplumbanes (R_3PbH , R_2PbH_2) form in reactions of dialkyl- or trialkylhaloplumbanes with LiAlH_4 in ethers (Me_2O or monoglyme) at -60 to -110°C in up to 90% yield, e.g.:



where R = Me, Et, i-Pr, n-Bu, C_6H_{11} .

Potassium tetrahydroborate reduces⁴ trialkylhaloplumbanes in liq NH_3 :



where R = Me, Et, i-Pr, n-Bu. Complex hydride reactions with alkyllead halides are preferred syntheses of alkylplumbanes.

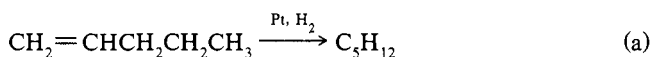
(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of the Main Groups I–IV*, Elsevier, Amsterdam, 1971.
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1.6.6. by Industrial Processes

1.6.6.1. Involving Compounds of Carbon.

Reactions of H_2 or H_2 sources (e.g., Zn-HCl) with alkenes, alkynes, arenes, ketones, nitriles, carboxylic acids and esters are used industrially for C—H bond formation^{1–8}. Heterogeneous reaction catalysts (e.g., Ni, Pt, Pd, Fe, Ni—Cu) are used, e.g.:

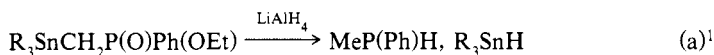


1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 111

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, Amsterdam, 1971.
2. W. L. Jolly, J. E. Drake, *Inorg. Synth.* 7, 34 (1966).
3. E. J. Kupchik, in *Organotin Compounds*, Vol. 1, A. K. Sawyer, ed., Marcel Dekker, New York, 1971, p. 7.
4. A. G. Davies, P. J. Smith, *Adv. Inorg. Chem. Radiochem.*, 23, 1 (1980).

1.6.5.4.3. from Other Derivatives.

The Sn—C bond in stannylmethylphosphonate is cleaved by LiAlH_4 :



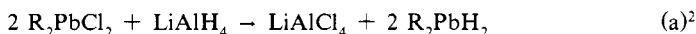
where R = Me, Et, Ph.

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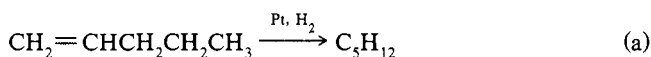
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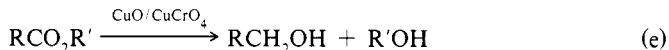
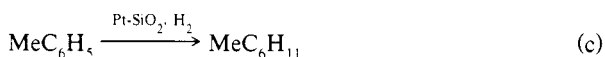
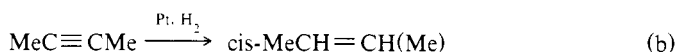
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1.6.6. by Industrial Processes

1.6.6.1. Involving Compounds of Carbon.

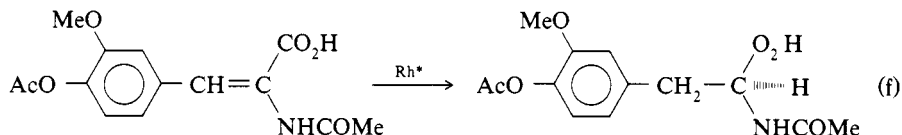
Reactions of H_2 or H_2 sources (e.g., Zn-HCl) with alkenes, alkynes, arenes, ketones, nitriles, carboxylic acids and esters are used industrially for C—H bond formation^{1–8}. Heterogeneous reaction catalysts (e.g., Ni, Pt, Pd, Fe, Ni—Cu) are used, e.g.:



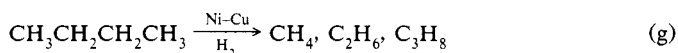


Reactions proceed at $> 25^\circ\text{C}$ ($25\text{--}300^\circ\text{C}$) at $> 10^3 \text{ Nm}^{-2}$ of H_2 .

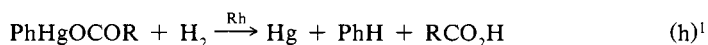
Examples of hydrogenation using homogeneous catalysts in moderate-scale industrial syntheses exist. Such catalysts are more selective and involve milder reaction conditions (i.e., 25°C and ca. 10^2 Pa H_2) than their heterogeneous counterparts^{4,6}. Asymmetric hydrogenation of a prochiral amino acid using chiral Rh catalysts yields L-dopa in high optical purity^{9,10}:



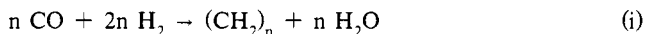
where $\text{Rh}^* = [\text{Rh}\{\text{S,S-}[\text{Ph}_2\text{P}(\text{Me})\text{C}_3\text{H}_4(\text{Me})\text{PPh}_2]\} 1,5\text{-C}_8\text{H}_{12}]\text{Cl}$. Reactions in which H_2 formally cleaves C—C bonds occur in hydrogenolysis processes^{2,4}. Heterogeneous catalysts are used, e.g.:



These reactions are discussed in treatises on organic chemistry. Hydrogenolysis of metal- or nonmetal-carbon bonds are used for small-scale specialty chemical syntheses:



Hydrogen reacts with CO in the presence of catalysts to produce hydrocarbon products ranging from CH_3OH and CH_4 to fuel oils^{6,11–16}:



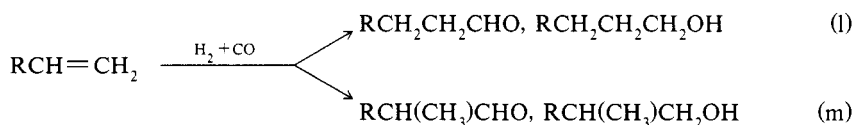
Products obtained depend on reaction conditions. Using $\text{Pd-La}_2\text{O}_3$ or $\text{Zn-Cr}_2\text{O}_3$ as catalysts, CH_3OH is the main product^{11,13}:



Over Ni at $500\text{--}700^\circ\text{C}$, principally CH_4 forms¹¹. Other transition-metal catalysts result in higher yields of $\text{C}_{>1}$ products. Ethylene glycol is produced effectively from CO and H_2 using homogeneous Rh catalysts:

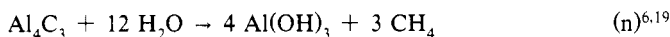


Hydroformylation, the addition of CO and H_2 to an alkene^{6,14,16–18}, occurs with homogeneous¹⁸ [e.g., $\text{RhCl}(\text{PPh}_3)_3$, $\text{HCo}(\text{CO})_4$], heterogeneous¹⁸ (e.g., Ni, Co, Fe, Rh) or supported catalysts^{3,14} [e.g., $\text{Rh}(\text{CO})_2\text{Cl}$ on SiO_2] to form alcohols and/or aldehydes:

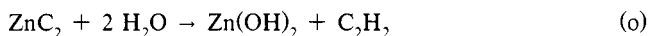


Aldehydes form prior to alcohols. Both branched and linear isomers form. Depending on the alkene substrate, reaction conditions, and catalyst selected, conditions selective for specific compound synthesis can be found^{15,17,18}.

Carbide hydrolysis is used to produce CH_4 and/or C_2H_2 in limited, special situations. Aluminum methanide hydrolyzes to form CH_4 :



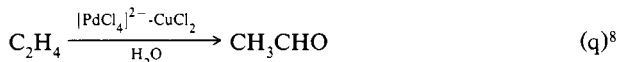
Electropositive metal (Cu, Zn, Al) acetylide hydrolysis produces C_2H_2 , e.g.:



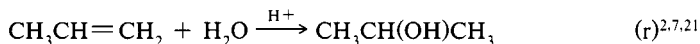
Protonation of aq $[\text{CN}]^-$ is a route^{6,20} to HCN :



Addition of protonic reagents to $\text{C}=\text{C}$ and/or $\text{C}\equiv\text{C}$ bonds is a route to $\text{C}-\text{H}$ bond-containing products^{2,7,21-23}. Acetaldehyde is produced by hydrolysis of C_2H_4 in the presence of catalysts:



Hydrolysis or alcoholysis occurs with mineral acid catalysts:



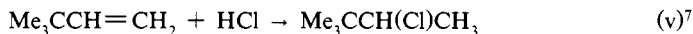
Reaction of alkenes with conc H_2SO_4 is a major route to sulfonates^{7,21}:



Addition of HCN to alkenes, in the presence of heterogeneous metal catalysts, produces substituted nitriles²³.



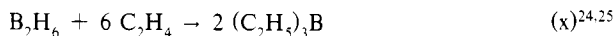
Hydrogen halide addition to alkenes and alkynes yields organohalides:



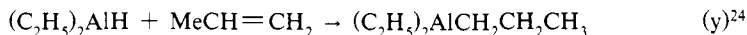
Halide addition to the most substituted carbon occurs [Eq. (v)], except in cases of radical reaction promotion, in which case addition of halide to the least substituted carbon is observed:



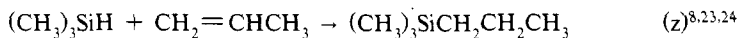
Addition of nonmetal- or metal-H bonds to $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bonds result in $\text{C}-\text{H}$ bond formation and production of organoelement products. Boranes:



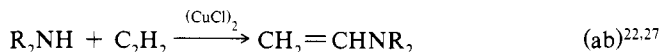
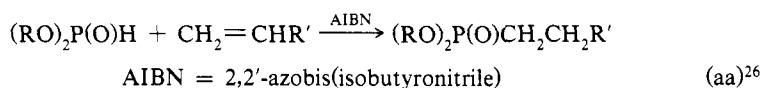
alanes:



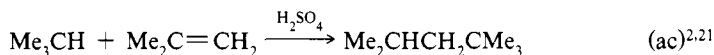
and silanes add directly to form organo derivatives, e.g.:



Reactions of silanes are often best catalyzed by hydrosilation catalysts⁸ such as Pt or Pd. Similarly, C—H bonds are formed in the addition of phosphines or amines to C=C or C≡C bonds. Reactions are catalyzed (acid, base, or metal) or free radical promoted, e.g.:

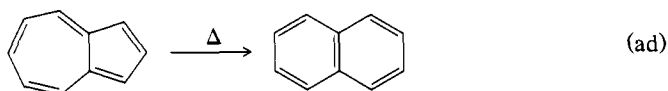


Carbon-hydrogen bonds add to alkenes or alkynes, e.g., iso-butane adds to iso-butene in the presence of conc H_2SO_4 :

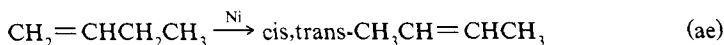


Such reactions are important in fuel-upgrading processes.

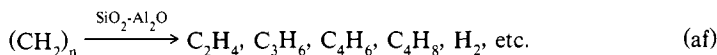
Hydride, either binary or complex, reductions of organic functional groups are expensive routes to C—H bonds, consequently such reactions are used only for specialty chemical and expensive product (pharmaceuticals, etc.) synthesis. Reactions as described in §1.6.4 and 1.6.5 are used. Commonly used reactions involve NaH, KH, boranes, alanes, silanes and occasionally stannanes. Detailed discussions of hydride reductions can be found in standard treatises on organic chemistry^{2,4,21,24,25,27}. Molecular rearrangement:



and/or isomerizations are important in petroleum refining and industrial chemical processes^{2,3,7,21}:



These, along with the molecule degradation and reformation processes of thermal and catalytic cracking^{2,3,7,16}, e.g.:



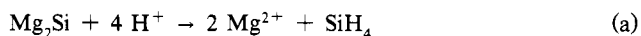
involve formation of new C—H bonds, albeit often in nonspecific reaction processes.

(A.D. NORMAN)

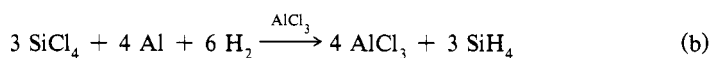
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20. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
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1.6.6.2. Involving Compounds of Silicon.

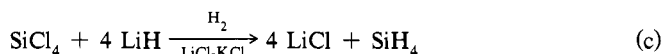
Silane is prepared industrially by the reaction of Mg_2Si with strong protonic acids^{1,2} such as H_3PO_4 or H_2SO_4 :



by the reaction of H_2 with SiCl_4 and Al in an AlCl_3 melt¹:



or by the reaction of H_2 with SiCl_4 and LiH or NaH in an LiCl-KCl eutectic^{1,3,4}:



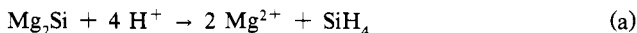
The latter two methods are preferred because they are adapted to the continuous production of SiH_4 .

1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 115
 1.6.6. by Industrial Processes

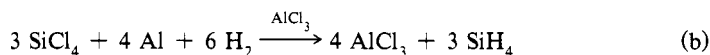
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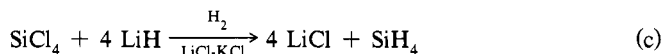
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or by the reaction of H_2 with SiCl_4 and LiH or NaH in an LiCl–KCl eutectic^{1,3,4}:



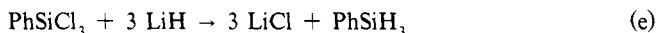
The latter two methods are preferred because they are adapted to the continuous production of SiH_4 .

Trichlorosilane is prepared from reaction of Si with anhyd HCl at 400°C:

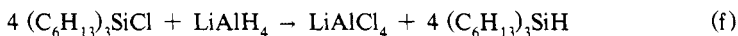


Along with alkylsilanes, including MeSiCl_2H , it is produced from the reaction of MeCl with a hot Cu-Si mixture⁵.

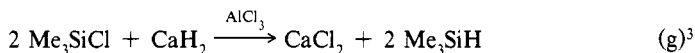
Organosilanes for commercial use are prepared by either LiH or LiAlH_4 reduction of the corresponding chlorosilanes, e.g., PhSiH_3 :



or $(\text{C}_6\text{H}_{13})_3\text{SiH}$:



Mono-, di- and triorganosilanes produced by these methods include RSiH_3 ($\text{R} = \text{C}_5\text{H}_{11}$, Ph , C_6H_{13}), R_2SiH_2 ($\text{R} = \text{Et}$, Ph) and R_3SiH ($\text{R} = \text{Et}$, C_6H_{13} , EtO , and $n\text{-Bu}$)^{1,5}. Calcium hydride reduction of Me_3SiCl in the presence of AlCl_3 yields Me_3SiH :

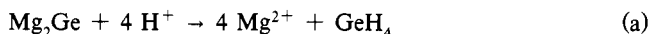


(A.D. NORMAN)

1. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
2. F. Feher, D. Schinkitz, J. Schaaf, *Z. Anorg. Allg. Chem.*, **383**, 303 (1971).
3. E. G. Rochow, in *Comprehensive Inorganic Chemistry*, Vol. 2, A. F. Trotman-Dickenson, ed., Pergamon Press, Oxford, 1973, p. 1323.
4. A. M. Pavlov, G. N. Bodyagin, I. L. Agafonov, *Tr. Khim. Khim. Techol.*, 175 (1967); *Chem. Abstr.*, **78**, 83,822 (1969).
5. D. A. Armitage, in *Comprehensive Organometallic Chemistry*, Vol. 2, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 1.

1.6.6.3. Involving Compounds of Germanium.

Germane is prepared in large quantities by reaction of strong protonic acids¹ with Mg_2Ge :



Lithium tetrahydroaluminate reduction of organochlorogermanes is used for preparation of limited (kilogram) quantities of selected organogermanes, e.g., Me_3GeH and Ph_3GeH :



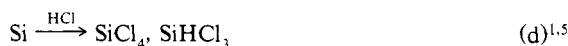
where $\text{R} = \text{Me}$, Ph .

(A.D. NORMAN)

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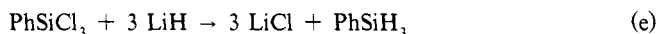
116 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
 1.6.6. by Industrial Processes

Trichlorosilane is prepared from reaction of Si with anhyd HCl at 400°C:

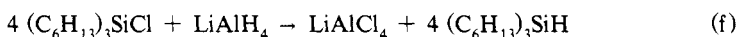


Along with alkylsilanes, including MeSiCl_2H , it is produced from the reaction of MeCl with a hot Cu-Si mixture⁵.

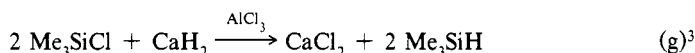
Organosilanes for commercial use are prepared by either LiH or LiAlH_4 reduction of the corresponding chlorosilanes, e.g., PhSiH_3 :



or $(\text{C}_6\text{H}_{13})_3\text{SiH}$:



Mono-, di- and triorganosilanes produced by these methods include RSiH_3 ($\text{R} = \text{C}_5\text{H}_{11}$, Ph , C_6H_{13}), R_2SiH_2 ($\text{R} = \text{Et}$, Ph) and R_3SiH ($\text{R} = \text{Et}$, C_6H_{13} , EtO , and $n\text{-Bu}$)^{1,5}. Calcium hydride reduction of Me_3SiCl in the presence of AlCl_3 yields Me_3SiH :

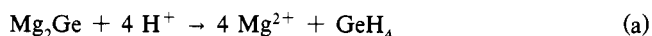


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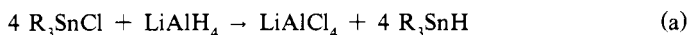
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(A.D. NORMAN)

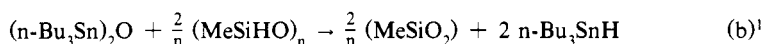
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1.6.6.4. Involving Compounds of Tin.

Specialty chemical quantities of organostannanes are prepared by LiAlH_4 reduction of the corresponding chlorostannanes¹:



where R = Et, n-Bu, Ph. Poly(methylhydrido)siloxane reduction of $(\text{n-Bu}_3\text{Sn})_2\text{O}$ forms n-Bu₃SnH:



(A.D. NORMAN)

1. A. G. Davies, in *Comprehensive Organometallic Chemistry*, Vol. 2, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, p. 519.

1.6.7. The Synthesis of Deuterium Derivatives

1.6.7.1. by Interconversion of Deuterated Compounds

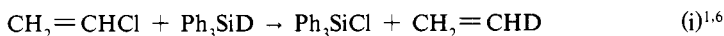
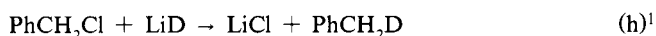
1.6.7.1.1. Involving Carbon Compounds.

Descriptions of C—D bond formation are found in treatises on synthetic organic chemistry¹⁻⁵, e.g., in the complex deuteride reductions:



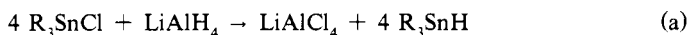
Some reactions proceed directly to products [e.g., Eqs. (a), (b)]; however, often the final product arises after D₂O hydrolysis of an intermediate borane, boronate or aluminate species.

Binary ionic (e.g., NaD) or covalent (e.g., Me₂SiD₂) hydrides are reductants for C—D bond formation^{1,6}, e.g.:

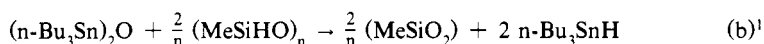


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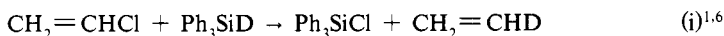
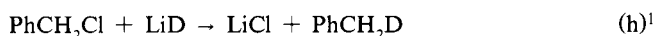
1.6.7.1.1. Involving Carbon Compounds.

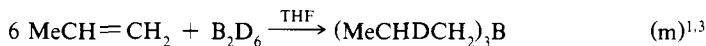
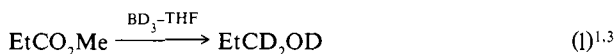
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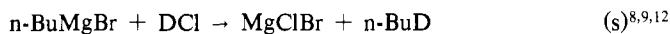
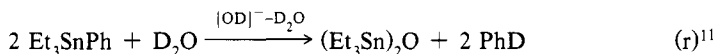
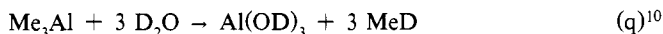
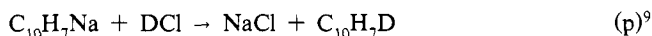
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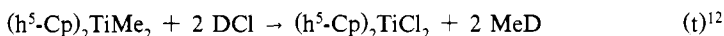


Hydride reductions can be selective and produce products in high isotopic yields.

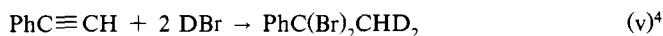
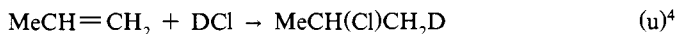
Carbides, carbanionic or metalated carbon compounds react with protonic acids, e.g., D_2O or DCl , forming deuteriocarbon compounds:



Reaction of complex metal species can be used also:



Deuterium halides (DCl , DBr) add to alkenes or alkynes:



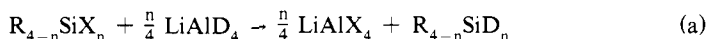
(A.D. NORMAN)

1. A. Hajós, *Complex Hydrides*, Elsevier, Amsterdam, 1979.
2. C. A. Buehler, D. E. Pearson, *Survey of Organic Syntheses*, Vol. 2, Wiley-Interscience, New York, 1977.
3. H. C. Brown, *Boranes in Organic Chemistry*, Cornell Univ. Press, Ithaca, NY, 1972.
4. A. I. Shatenshtein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.
5. A. Murray, III, D. L. Williams, *Organic Syntheses with Isotopes*, Part II, Wiley-Interscience, New York, 1958.
6. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
7. A. K. Holliday, G. Hughes, S. M. Walker, in *The Chemistry of Carbon*, Pergamon Press, Oxford, 1973, Ch. 13, p. 1173.
8. D. J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York, 1965.
9. D. Bethell, in *Comprehensive Organic Chemistry*, D. Barton, W. D. Ollis, eds., Vol. 1, J. F. Stoddard, ed., Pergamon Press, Oxford, 1979, p. 411.
10. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
11. A. G. Davies, P. J. Smith, *Adv. Inorg. Chem. Radiochem.* 23, 1 (1980).
12. E. Klei, J. H. Teichen, *J. Organomet. Chem.*, 188, 97 (1980).

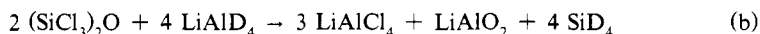
- 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 119
 1.6.7. The Synthesis of Deuterium Derivatives
 1.6.7.1. by Interconversion of Deuterated Compounds

1.6.7.1.2. Involving Silanes.

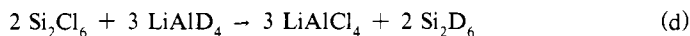
Lithium tetrahydroaluminate-d₄ or LiBD₄ reductions of halosilanes or oxysilanes are preferred routes to alkyl, aryl or unsubstituted deuteriosilanes¹⁻⁴:



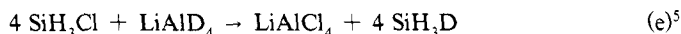
where R = H, alkyl, aryl; n = 1-4;



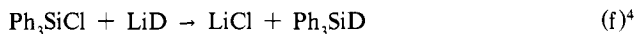
Similarly, higher deuterio silanes form:



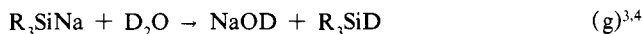
Reaction of LiAlD₄ with halohydrides allows synthesis of specifically labeled mixed H-D compounds:



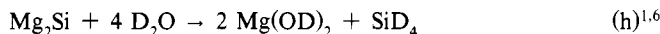
Alkali-metal deuteride reduction of halosilanes produces deuteriosilanes readily, but yields are less than from LiAlD₄ halosilane reactions:



Alkali-metal silyls react with D₂O:



Silicides with D₂O or DCl-D₂O yield SiD₄, along with lesser quantities of higher deuteriosilanes, i.e., Si₂D₆, Si₃D₈, and n-Si_nD₁₀:



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5. H. J. Meal, M. R. Wilson, *J. Chem. Phys.*, 24, 385 (1956).
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Lithium tetrahydroaluminate-d₄ or LiBD₄ reduction of halogermanes and oxygermanes are preferred syntheses of deuteriogermaenes, e.g.:



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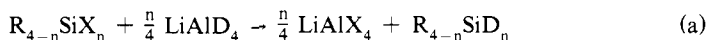


Reaction of LiAlD₄ with GeHCl₃ yields the mixed hydro-deuterio product in high isotopic purity and specificity:

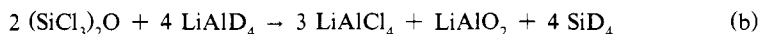
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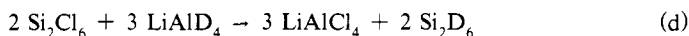
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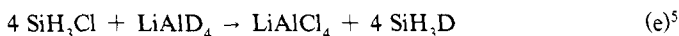
where R = H, alkyl, aryl; n = 1-4;



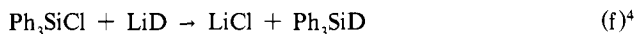
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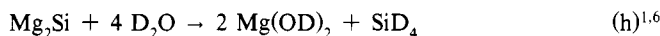
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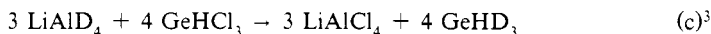
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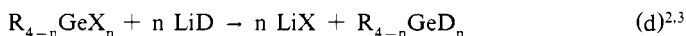
where n = 1-4; R = alkyl, aryl;



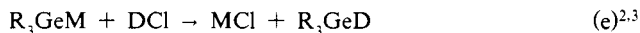
Reaction of LiAlD₄ with GeHCl₃ yields the mixed hydro-deuterio product in high isotopic purity and specificity:



Aklali-metal deuteride reduction of halogermanes yields deuteriogermanes but not in reactions preferred over those using complex hydrides:

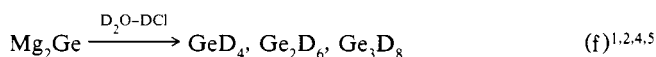


Reaction of germanide salts with D_2O or DCl yields deuteriogermanes in high isotopic purity:



where R = alkyl, aryl; M = Li, Na, K.

Germane- d_4 and lesser amounts of higher germanes form upon DCl - D_2O treatment of Mg_2Ge :

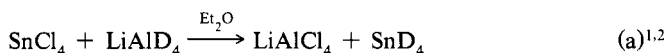


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4. L. P. Lindeman, M. K. Wilson, *Z. Phys. Chem. (Leipzig)*, 929 (1956).
5. A. H. Zeltman, G. C. Fitzgibbon, *J. Am. Chem. Soc.*, 76, 2021 (1954).

1.6.7.1.4. Involving Stannanes.

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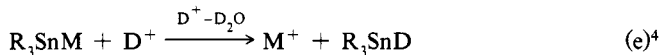
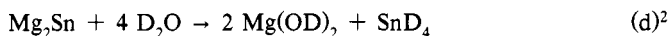


where R = alkyl, aryl. Diethylalane- d_1 reacts similarly with halostannanes forming deuterated products:



where $n = 1-3$; R = alkyl, aryl.

Solvolysis of stannides with deuterated hydroxylic reagents yields deuteriostannanes. Stannane- d_4 and alkyl- and arylstannanes form:



where R = aryl, alkyl; M = Li, Na.

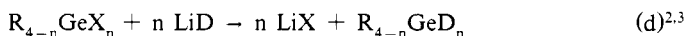
Tri- n -butylstannane, upon treatment with EtMgCl followed by D_2O , forms⁴ $n\text{-Bu}_3\text{SnD}$.

(A.D. NORMAN)

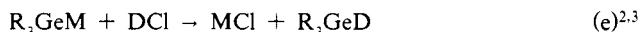
- 120 1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb
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Aklali-metal deuteride reduction of halogermanes yields deuteriogermanes but not in reactions preferred over those using complex hydrides:

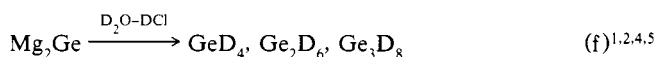


Reaction of germanide salts with D_2O or DCl yields deuteriogermanes in high isotopic purity:



where R = alkyl, aryl; M = Li, Na, K.

Germane- d_4 and lesser amounts of higher germanes form upon DCl - D_2O treatment of Mg_2Ge :

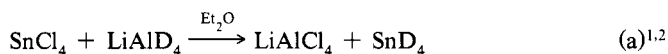


(A.D. NORMAN)

1. A. D. Norman, J. R. Webster, W. L. Jolly, *Inorg. Synth.* 11, 170 (1968).
2. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
3. M. Lesbre, D. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971.
4. L. P. Lindeman, M. K. Wilson, *Z. Phys. Chem. (Leipzig)*, 929 (1956).
5. A. H. Zeltman, G. C. Fitzgibbon, *J. Am. Chem. Soc.*, 76, 2021 (1954).

1.6.7.1.4. Involving Stannanes.

Lithium tetrahydroaluminate- d_4 and LiBD_4 reductions of halostannanes constitute preferred syntheses of deuteriostannanes, e.g.:

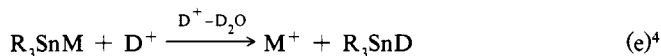
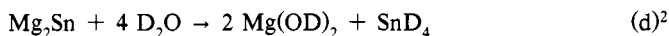


where R = alkyl, aryl. Diethylalane- d_1 reacts similarly with halostannanes forming deuterated products:



where $n = 1-3$; R = alkyl, aryl.

Solvolysis of stannanes with deuterated hydroxylic reagents yields deuteriostannanes. Stannane- d_4 and alkyl- and arylstannanes form:



where R = aryl, alkyl; M = Li, Na.

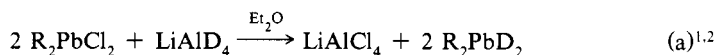
Tri-*n*-butylstannane, upon treatment with EtMgCl followed by D_2O , forms⁴ $n\text{-Bu}_3\text{SnD}$.

(A.D. NORMAN)

1. A. D. Norman, J. R. Webster, W. L. Jolly, *Inorg. Synth.* 11, 170 (1968).
2. E. Wiberg, E. Amberger, *Hydrides of Elements of the Main Groups I-IV*, Elsevier, Amsterdam, 1971.
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4. E. J. Kupchik, in *Organotin Compounds*, Vol. 1, A. K. Sawyer, ed., Marcel Dekker, New York, 1971, p. 7.

1.6.7.1.5. Involving Plumbanes.

Reactions of LiAlD_4 with di- or trialkylhaloplumbanes in ether (Me_2O or monoglyme) at -60°C to -110°C can produce alkyldeuterioplumbanes:



(A.D. NORMAN)

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1.6.7.2. by Isotopic Enrichment Using Chemical Reactions

1.6.7.2.1. of Carbon Compounds.

Direct exchange of $\text{C}-\text{H}$ bonds with D_2 can yield $\text{C}-\text{D}$ bonds. Alkane $\text{C}-\text{H}$ exchange occurs on activated metal (e.g., Ni or Pt) surfaces¹:



Aromatic $\text{C}-\text{H}$ bond exchange occurs similarly but more slowly¹. Benzene- D_2 exchange occurs in the presence of metal hydrides such as $(\text{h}^5\text{-C}_5\text{H}_5)_3\text{TaH}_3$, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{NbH}_3$, or $\text{h}^3\text{-C}_3\text{H}_5\text{CoH}[\text{P}(\text{OMe})_3]_3$ ¹⁻³.



Hydrocarbons undergo metal or non-metal halide-catalyzed $\text{C}-\text{H}$ bond exchange with strong deuterio acids. Reactions are accelerated by metal-halide catalysts such as AlCl_3 , AlBr_3 , FeBr_3 or TiBr_4 :



In strong acid media, i.e., DF or DBr , aromatic $\text{C}-\text{H}$ bond exchange occurs:



Deuteriosulfuric acid exchanges slowly with C_2H_4 or saturated hydrocarbons:



In the presence of transition-metal hydride catalysts, olefin exchange also can occur⁴:

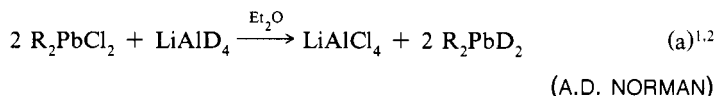


1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb 121
 1.6.7. The Synthesis of Deuterium Derivatives

1. A. D. Norman, J. R. Webster, W. L. Jolly, *Inorg. Synth.* 11, 170 (1968).
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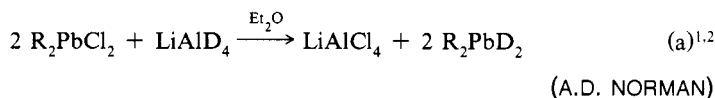


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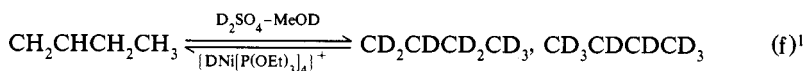
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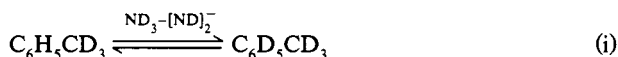
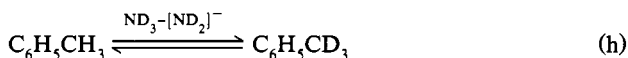
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Hydrocarbon C—H bond exchange, in reactions involving them as protonic acids, occurs readily. Ease of reaction depends on the acidity of the hydrocarbon. Exchange between aliphatic hydrocarbons and ND₃ in the presence of [ND₂][−] catalyst occurs:



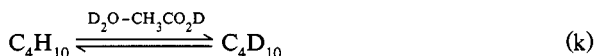
Exchange of the aliphatic C—H bonds in C₆H₅CH₃ occurs ca. 250 times faster than that of the aromatic C—H bonds^{5,7}:



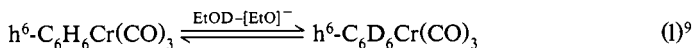
Exchange of more acidic hydrocarbons, e.g., C₂H₂ or C₃H₆ occurs readily in D₂O with an [OD][−] catalyst⁵:



however, most alkanes undergo sufficient activation for rapid exchange only in the presence of metal catalysts (e.g., Pt, Ni) and at elevated T^{1,8}:



The coordination of aromatic rings to transition metals, such as in h⁶-C₆H₆Cr(CO)₃, increases C—H bond acidity enough to allow C—H bond exchange with EtOD:



(A.D. NORMAN)

1. S. C. Davis, K. J. Klabunde, *Chem. Rev.*, **82**, 153 (1982).
2. B. R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979).
3. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980.
4. D. M. Roundhill, *Adv. Organomet. Chem.*, **13**, 273 (1975).
5. A. I. Shatenstein, *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, Consultants Bureau, New York, 1962.
6. L. F. Fieser, M. Fieser, *Advanced Organic Chemistry*, Reinhold, New York, 1961.
7. W. L. Jolly, *The Inorganic Chemistry of Nitrogen*, Benjamin, New York, 1964.
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1.6.7.2.2. of Silanes.

Silane exchanges with DCl in the presence of AlCl₃:



Competing reactions forming chlorosilanes occur also. Alkylsilanes exchange similarly, although C—Si bond cleavage also occurs.

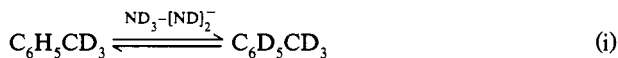
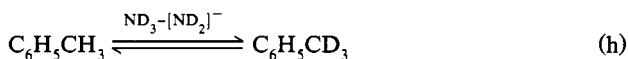
Silane reactions with D₂ under thermal, photolytic or silent electric discharge conditions result in H—D exchange. These reactions are not usually synthetically viable^{1,2}:

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 1.6.7. The Synthesis of Deuterium Derivatives
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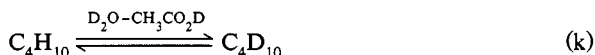
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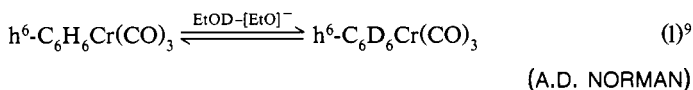
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Intermolecular exchange between silanes in the presence of an H_2PtCl_6 catalyst occurs at 100°C :



(A.D. NORMAN)

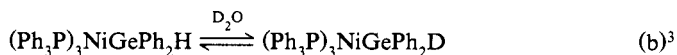
1. E. A. V. Ebsworth, *Volatile Silicon Compounds*, Pergamon Press, Oxford, 1963.
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3. D. M. Roundhill, *Adv. Organomet. Chem.*, 13, 273 (1975).

1.6.7.2.3. of Germanes.

Germanes are often sufficiently acidic¹⁻³ that their exchange with deuterio solvents can be an effective route to $\text{Ge}-\text{D}$ bonds:



These reactions seldom offer advantages over hydride reductions, except if GeD bond formation in a complex molecule, such as a germyl-metal species, is involved:



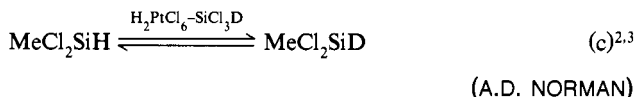
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1. T. Birchall, W. L. Jolly, *Inorg. Chem.*, 5, 2177 (1966).
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1.6. Formation of Bonds between Hydrogen and C, Si, Ge, Sn, Pb	123
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1.6.7.2. by Isotopic Enrichment Using Chemical Reactions	



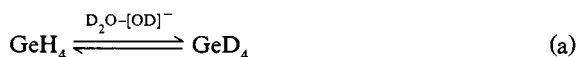
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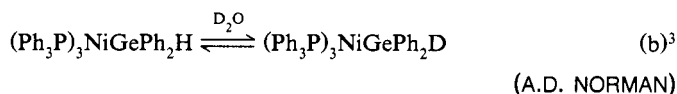
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2. E. Wiberg, E. Amberger, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971.
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Germanes are often sufficiently acidic¹⁻³ that their exchange with deuterio solvents can be an effective route to Ge—D bonds:



These reactions seldom offer advantages over hydride reductions, except if GeD bond formation in a complex molecule, such as a germyl-metal species, is involved:



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3. D. M. Roundhill, *Adv. Organomet. Chem.*, **13**, 273 (1975).

1.7. Formation of Bonds between Hydrogen and Elements of Group IIIB (B, Al, Ga, In, Tl)

1.7.1. Introduction

The chemistry described in this section is dominated by that of boron and to a lesser extent of Al. The hydride chemistry of Ga and, especially, of In and Tl is developed only to a limited extent.

There are few useful reactions in which new B—H bonds are formed. Although the formation of boranes from the protolysis of borides or the reduction of boron compounds with H_2 , either in electrical discharges or in the presence of active metals, have historical importance, these methods have no importance or utility today. Indeed, the preparation of boranes is so dominated by the single common starting material, the tetrahydroborate ion, that the only important reactions in which B—H bonds are formed are those in which hydride ion either reduces species with B—O or B—halogen bonds to form boranes or adds to trifunctional boron compounds to form hydroborates.

There are other reactions in which, although in the strictest interpretation new B—H bonds are not formed, B—H—B bridge bonds are formed from B—H terminal bonds. The formation of B—H—B bridge bonds from B—H bonds is considered B—H bond formation for the purpose of this treatment.

The arrangement of this section patterns that of others in these volumes; however, for the group IIIB elements this is not as useful because the important chemical reactions in which B—H bonds are formed from other B—H bonds are not highlighted. Some of the important reactions in which there is no net increase in the number of B—H bonds are found in §1.7.5.1.

Except for the tetrahydroaluminates and -gallates the chemistry of element—H bond formation for the congeners of B is rare. Most electron-pair donor base adducts of AlH_3 and GaH_3 are derived from $LiAlH_4$ and $LiGaH_4$, respectively. The hydride chemistry of In and Tl is sparse. The species $LiInH_4$ and $LiTlH_4$ exist; however, evidence for the existence of the normal hydrides InH_3 and TlH_3 , is not convincing.

Reviews describing H—group III element bond formation are listed in refs. 1–14.

(L. BARTON)

1. A. Stock, *The Hydrides of Boron and Silicon*, Cornell Univ. Press, Ithaca, NY, 1933.
2. H. I. Schlesinger, A. B. Burg, *Chem. Rev.*, **32**, 1 (1942).
3. R. M. Adams, in *Borax to Boranes*, D. L. Martin, ed., Advances in Chemistry Series No. 32, American Chemical Society, Washington, DC, 1961, p. 66.
4. R. M. Adams, ed., *Boron, Metalloboron Compounds and Boranes*, Interscience, New York, 1964.
5. E. C. Ashby, *Adv. Inorg. Chem. Radiochem.*, **8**, 283 (1966).
6. L. A. Sheka, I. S. Chaus, T. T. Mityureva, *The Chemistry of Gallium*, Elsevier, Amsterdam, 1966, Ch. 2.

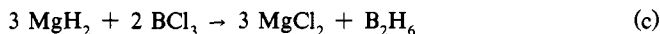
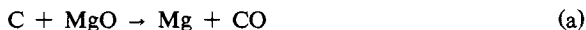
7. R. T. Holtzman, R. L. Hughes, I. C. Smith, E. W. Lawless, *Production of the Boranes and Related Research*, Academic Press, New York, 1967.
8. N. N. Greenwood, in *New Pathways in Inorganic Chemistry*, E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe, eds., Cambridge Univ. Press, Cambridge, 1968, Ch. 3.
9. R. W. Parry, M. K. Walter, *Prep. Inorg. React.*, 5, 45 (1968).
10. B. D. James, M. G. H. Wallbridge, *Prog. Inorg. Chem.*, 11, 99 (1970).
11. H. D. Johnson II, S. G. Shore, *Top. Curr. Chem.* 15, 88 (1970).
12. S. G. Shore, in *Boron Hydride Chemistry*, E. L. Muetterties, ed., Academic Press, New York, 1975, Ch. 3.
13. A. B. Burg, *Chem. Tech.*, Jan., 1977, p. 50.
14. S. G. Shore, in *Rings, Cages, Clusters and Polymers of the Main Group Elements*, A. H. Cowley, ed., ACS Symposium Series No. 232, American Chemistry Society, Washington, DC 1983, p. 1.

1.7.2. from the Elements.

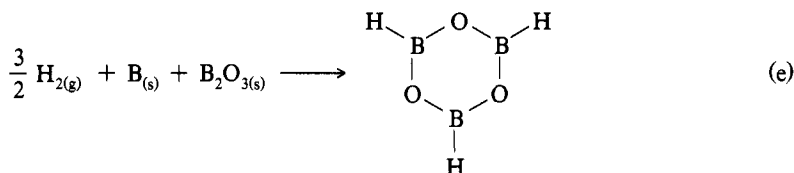
The direct reaction between elemental boron and H_2 gas has limited utility¹; e.g., Mg_2B_3 , which contains elemental boron, does not react with H_2 at high T. However the reaction between boron and H_2 at $840^\circ C$ forms² only traces of B_2H_6 , and H_2 reacts little with boron powder³. Thermodynamic calculations based on free energy minimization for the chemical-vapor deposition of boron from BX_3-H_2 mixtures ($X = Cl, Br$) at 1000–1900 K and 0.101 MPa indicate low borane (BH_3) conc at equilibrium, but traces of HBX_2 are predicted in these T ranges⁴.

An electrochemical process in which H_2 gas is fed into an electrolyzed metal-halide mixture with a boron anode⁵ yields B_2H_6 . The reaction proceeds via the intermediacy of metal hydride.

A cyclic process using as raw materials H_2 , coke, MgO and BCl_3 is available⁶. The reaction proceeds through the intermediacy of MgH_2 formed at the cathode and boron halide formed at the anode. These react together in the melt with the stoichiometry described in §1.7.4.1.1:



The B—H bond is formed from the reaction between H_2 and boron monoxide⁷ (B_2O_2) or in systems in which the latter is prepared in situ^{8–10}. When H_2 is passed over a mixture⁸ of boron and boric oxide at $1200^\circ C$:



The product boroxine ($B_3H_3O_3$) disproportionates when condensed at 77 K and subsequently warmed to RT. Diborane and boric oxide are formed:

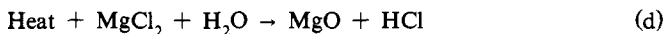
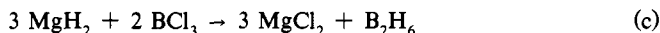
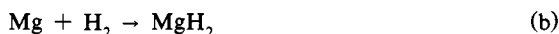
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8. N. N. Greenwood, in *New Pathways in Inorganic Chemistry*, E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe, eds., Cambridge Univ. Press, Cambridge, 1968, Ch. 3.
9. R. W. Parry, M. K. Walter, *Prep. Inorg. React.*, 5, 45 (1968).
10. B. D. James, M. G. H. Wallbridge, *Prog. Inorg. Chem.*, 11, 99 (1970).
11. H. D. Johnson II, S. G. Shore, *Top. Curr. Chem.* 15, 88 (1970).
12. S. G. Shore, in *Boron Hydride Chemistry*, E. L. Muetterties, ed., Academic Press, New York, 1975, Ch. 3.
13. A. B. Burg, *Chem. Tech.*, Jan., 1977, p. 50.
14. S. G. Shore, in *Rings, Cages, Clusters and Polymers of the Main Group Elements*, A. H. Cowley, ed., ACS Symposium Series No. 232, American Chemistry Society, Washington, DC 1983, p. 1.

1.7.2. from the Elements.

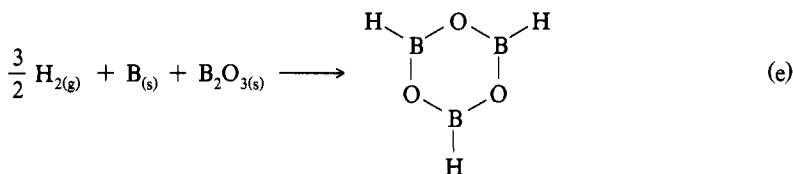
The direct reaction between elemental boron and H_2 gas has limited utility¹; e.g., Mg_2B_3 , which contains elemental boron, does not react with H_2 at high T. However the reaction between boron and H_2 at 840°C forms² only traces of B_2H_6 , and H_2 reacts little with boron powder³. Thermodynamic calculations based on free energy minimization for the chemical-vapor deposition of boron from BX_3-H_2 mixtures ($X = Cl, Br$) at 1000–1900 K and 0.101 MPa indicate low borane (BH_3) conc at equilibrium, but traces of HBX_2 are predicted in these T ranges⁴.

An electrochemical process in which H_2 gas is fed into an electrolyzed metal-halide mixture with a boron anode⁵ yields B_2H_6 . The reaction proceeds via the intermediacy of metal hydride.

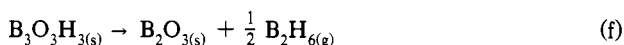
A cyclic process using as raw materials H_2 , coke, MgO and BCl_3 is available⁶. The reaction proceeds through the intermediacy of MgH_2 formed at the cathode and boron halide formed at the anode. These react together in the melt with the stoichiometry described in §1.7.4.1.1:



The B—H bond is formed from the reaction between H_2 and boron monoxide⁷ (B_2O_2) or in systems in which the latter is prepared in situ^{8–10}. When H_2 is passed over a mixture⁸ of boron and boric oxide at 1200°C:

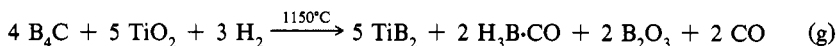


The product boroxine ($B_3H_3O_3$) disproportionates when condensed at 77 K and subsequently warmed to RT. Diborane and boric oxide are formed:

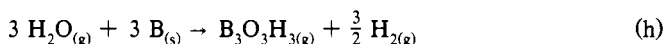


Reaction (f) also proceeds with first-order kinetics in the gas phase; the half-life of the process¹¹ is < 90 min.

Polymeric BO, prepared from the reaction between B_2O_3 and boron or carbon at 1150°C, B_2O_3 and B_4C at 1250°C, or MO_2 ($\text{M} = \text{Ti}, \text{Zr}$) and B_4C at 1200°C, reacts with H_2 at 1400°C to give, ultimately, diborane in ~10% yields⁹⁻¹¹. Similarly, when H_2 is passed over mixtures that form $\text{B}_2\text{O}_{2(\text{g})}$ in situ, B—H bonds are formed. The isolated B_2H_6 is formed via the intermediacy of $\text{B}_3\text{O}_3\text{H}_{3(\text{g})}$. When carbon is in the system, e.g., reaction mixtures $\text{C} + \text{B}_2\text{O}_3$ or $\text{TiO}_2 + \text{B}_4\text{C}$, the ultimate product is borane carbonyl^{9,10}. The stoichiometry for the latter process is:

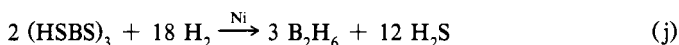
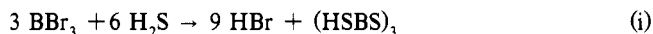


Boroxine is also formed when H_2O vapor is passed over elemental boron at 1150°C⁸:

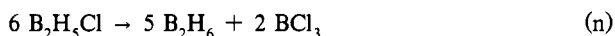
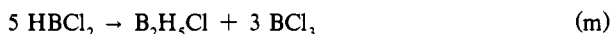


Diborane may be prepared¹² in yields of 40–50% by treatment of B_2O_3 with H_2 gas above 150°C at 75.8 MPa in the presence of Al and AlCl_3 . The hydrogenation proceeds through a chloroalane intermediate.

The hydrogenation of $(\text{HSBS})_3$ to B_2H_6 , with finely divided Ni as a catalyst, occurs in inert solvents¹³. The $(\text{HSBS})_3$ is prepared from H_2S and BBr_3 and the scheme is:



The first moderate-yield process for the formation of B—H bonds from the reaction of H_2 with boron halides utilizes passage of mixtures of H_2 and BCl_3 through an electrical discharge between Cu electrodes¹⁴. When H_2 : BCl_3 is 10 at 2.67×10^3 Pa, yields of $\leq 60\%$ B_2H_6 , based on BCl_3 consumed in 2 h, are available. This approach¹⁵ is more convenient when BBr_3 is used instead of BCl_3 . The lower volatility of the bromo species makes the process simpler and separation of products more convenient. This discharge process proceeds in steps¹⁶:

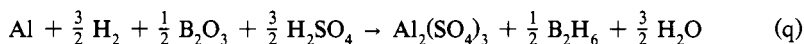
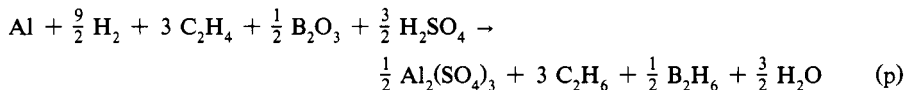
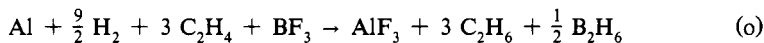


The major initially formed product is $\text{B}_2\text{H}_5\text{Cl}$, which disproportionates to BCl_3 and B_2H_6 on fractionation. The γ -irradiation-induced reaction between H_2 and BCl_3 does not form boranes¹⁷.

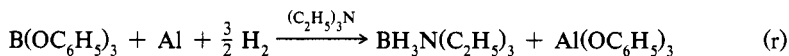
The thermal reaction between BCl_3 and H_2 at 300–450°C in the presence of granular, 20-mesh Al affords B_2H_6 in $\leq 60\%$ yields¹⁸. The 6:1 H_2 – BCl_3 mixture is passed through a heated reactor column. The similar reduction of BBr_3 with H_2 produces only

traces of B_2H_6 . An analogous process¹⁹ forms B_2H_6 in 8% yields when H_2 and BCl_3 are passed over Al_2Cu alloy at $450^\circ C$.

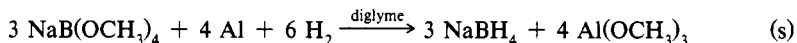
Hydrogenation of borates or boroxines at 81.1 MPa of H_2 in the presence of Al and $NaAlCl_4$ forms diborane^{20,21}:



Boric acid may be similarly reduced to B_2H_6 under basic conditions on a large scale. Hydrogen in the presence of Al reduces borates to boranes quantitatively. These boranes are trapped as the amine borane, e.g., phenylborate is dissolved in triethylamine and to the solution is added activated Al powder and small amounts of $AlCl_3$ catalyst. The mixture is agitated at $180^\circ C$ for 1 h at 14.2 MPa of H_2 . Quantitative yields of the $(CH_3)_3NBH_3$ species are available from this process²² with a lower yield of $C_6N_5N(CH_3)_2BH_3$:



A similar process converts complex alkylborates to the tetrahydroborate ion:



The B—C bond may be reduced in the presence of H_2 at high P and T to afford boranes, e.g., alkylboranes²³ and arylboranes²⁴ are converted to organodiboranes and, in the presence of amines, to amine boranes²³, and also in processes²⁵ in which solid borane polymer is formed from liquid organoboranes and H_2 at $200^\circ C$. Partial hydrogenation of trialkylboranes to dialkylboranes is effected²⁶ by treatment of the borane with H_2 gas at 30.4 MPa and 120 – $200^\circ C$. Amine complexes of haloboranes are reduced by H_2 gas to R_3NBH_3 species and ultimately to diborane²⁷. Amine complexes of triorganoboranes are also converted to amineborane by reaction with H_2 gas²⁸. Finally, tetrahalodiboranes(4) are converted to the dihaloboranes by reaction with H_2 below $0^\circ C$. The H_2BX species disproportionate²⁹ to yield ultimately B_2H_6 and BX_3 .

This hydrogenolysis of compounds containing B—B bonds also may be extended to B_4H_{10} . One mol of B_4H_{10} reacts with 1 mol of H_2 to afford B_2H_6 , a reaction in which two new B—H bonds are formed³⁰:



Boron—H bonds may be formed from the reaction between alkali metals, H_2 and either BF_3 or trimethylborate. Low yields of B_2H_6 and $[BH_4]^-$ are available from the halide; however, reaction with $B(OCH_3)_3$ at $230^\circ C$ affords the $[BH(OCH_3)_3]^-$ ion³¹:



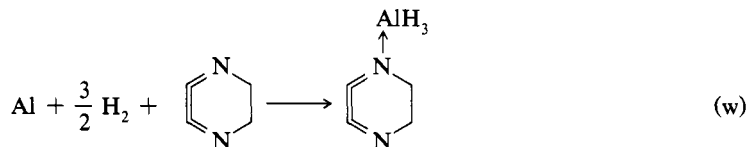
At higher T:



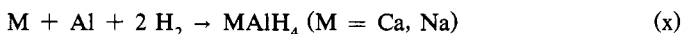
However, yields of B—H bond-containing products are low.

The Al—H bond forms by passage of an electrical discharge through $\text{Al}(\text{CH}_3)_3$ gas in the presence of $x\text{s H}_2$ at elevated T as the mixed methylaluminum hydrides³², $\text{Al}_2\text{H}_n(\text{CH}_3)_{6-n}$. The unsubstituted alane is formed as the $(\text{AlH}_3)_n$ polymer or as a base adduct from the same system³³; gaseous AlH_3 and Al_2H_6 are obtained^{34,35} by the passage of H_2 gas over an Al droplet at 1170–1250°C at low P.

Treatment of 1,4-diazabicyclo[2.2.2]octane in tetrahydrofuran (THF) with activated Al powder at 70°C under 34 MPa of H_2 forms³⁶ the Al—H bond as the amine alane:



The best route to Al—H bonds from the elements is the formation of tetrahydroaluminates, because these reagents are convenient to handle and may be used to prepare other alanes. The reaction between an alkali- or alkaline-earth metal and activated Al at 110–140°C in THF at 15.2–35.5 MPa H_2 affords the tetrahydroaluminate salt in quantitative yield^{37–40}:



Under similar conditions metal hydrides react with Al and H_2 to afford the Na^+ , Li^+ , K^+ and Cs^+ salts:



The most suitable solvents are THF for NaAlH_4 and LiAlH_4 , diglyme for KAlH_4 and toluene for CsAlH_4 .

Treatment of Na, Al and $\text{Al}(\text{C}_2\text{H}_5)_3$ with H_2 at ~33.4 MPa at 165°C in toluene for 10 h affords the hexahydroaluminate salt Na_3AlH_6 in 98% yield⁴¹.

Gallane, GaH_3 , is claimed⁴² from passage of an electrical discharge through mixtures of $\text{Ga}(\text{CH}_3)_3$ and H_2 ; however, these results are questioned⁴³. Exposure of H_2 and Ga to ~2300°C shows UV spectra⁴⁴ assigned to the GaH molecule, and passage of H_2 and Ga vapor at 926–1176°C into a time-of-flight mass spectrometer results³⁵ in weak spectra attributable to $[\text{GaH}_3]^+$. Similar evidence is available for the formation of InH_3 from its elements.

(L. BARTON)

1. A. Stock, *Hydrides of Boron and Silicon*, Cornell Univ. Press, Ithaca, NY, 1933, p. 42.
2. A. E. Newkirk, D. T. Hurd, *J. Am. Chem. Soc.*, **77**, 241 (1955).
3. G. V. Tsagareishvili, I. A. Bairamashvili, K. A. Oganezov, M. L. Tabutsidze, O. A. Tsagareishvili, *J. Less-Common Met.*, **82**, 131 (1981).
4. R. Naslain, J. Thebault, P. Hagemuller, C. Bernard, *J. Less-Common Met.*, **67**, 85 (1979).
5. E. Enk, J. Nickl, Ger. Pat. 1,092,890 (1960); *Chem. Abstr.*, **55**, 2687 (1961).
6. L. G. Dean, C. W. McCutcheon, A. C. Doumas, U.S. Pat. 3,024,091 (1962); *Chem. Abstr.*, **57**, 8198 (1962).
7. C. C. Clark, F. A. Kanda, J. A. King, U.S. Pat. 3,021,197 (1962); *Chem. Abstr.*, **56**, 13,810 (1962).
8. W. P. Shollette, R. F. Porter, *J. Phys. Chem.*, **67**, 177 (1963).
9. L. Barton, D. Nicholls, *Proc. Chem. Soc.*, 242 (1964).

10. L. Barton, D. Nicholls, *J. Inorg. Nucl. Chem.*, **28**, 1367 (1966).
11. L. Barton, *J. Inorg. Nucl. Chem.*, **30**, 1683 (1968).
12. T. A. Ford, G. H. Kalb, A. L. McClelland, E. L. Muetterties, *Inorg. Chem.*, **3**, 1032 (1964).
13. C. D. Barr, D. G. Hummel, U.S. Pat. 2,965,456 (1960); *Chem. Abstr.*, **55**, 22,737 (1961).
14. H. I. Schlesinger, A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).
15. A. Stock, H. Martini, W. Sutterlin, *Chem. Ber.*, **67B**, 396 (1934).
16. H. W. Myers, R. F. Putnam, *Inorg. Chem.*, **3**, 655 (1963).
17. A. J. Levy, J. Williamson, L. W. Steiger, *J. Inorg. Nucl. Chem.*, **17**, 26 (1961).
18. D. T. Hurd, *J. Am. Chem. Soc.*, **71**, 20 (1949).
19. V. I. Mikheeva, T. N. Dymova, *Zh. Neorg. Khim.*, **2**, 2530 (1957).
20. R. M. Adams, in *Boron, Metalloboron Compounds and Boranes*, R. M. Adams, ed., Interscience, New York, 1964, p. 562.
21. R. Köster, K. Ziegler, *Angew. Chem.*, **69**, 94 (1957).
22. E. C. Ashby, W. E. Foster, *J. Am. Chem. Soc.*, **84**, 3407 (1962).
23. R. Köster, *Angew. Chem.*, **69**, 94 (1957).
24. R. Köster, G. Bruno, P. Binger, *Justus Liebigs Ann. Chem.*, **644**, 1 (1961).
25. R. Köster, *Angew. Chem.*, **70**, 743 (1958).
26. Studiengesellschaft Kohle GmbH., Br. Pat. 854,919 (1960); *Chem. Abstr.*, **55**, 15,350 (1961).
27. R. M. Adams, in *Boron, Metalloboron Compounds and Boranes*, R. M. Adams, ed., Interscience, New York, 1964, p. 566.
28. R. Köster, K. Ziegler, *Angew. Chem.*, **69**, 94 (1957).
29. G. Urry, T. Wartik, H. I. Schlesinger, *J. Am. Chem. Soc.*, **74**, 5809 (1952).
30. H. I. Schlesinger, Univ. Chicago, Navy Contract N173-s-9280, Final Report (1945-46); see ref. 20, p. 560.
31. H. I. Schlesinger, H. C. Brown, A. E. Finholt, *J. Am. Chem. Soc.*, **75**, 205 (1953).
32. E. Wiberg, O. Stecher, *Angew. Chem.*, **52**, 372 (1939).
33. O. Stecher, E. Wiberg, *Chem. Ber.*, **75B**, 2003 (1942).
34. P. Briesacher, B. Siegel, *J. Am. Chem. Soc.*, **86**, 5053 (1964).
35. P. Briesacher, B. Siegel, *J. Am. Chem. Soc.*, **87**, 4257 (1965).
36. E. C. Ashby, *J. Am. Chem. Soc.*, **68**, 1882 (1964).
37. H. Clasen, *Angew. Chem.*, **73**, 322 (1961).
38. E. C. Ashby, *Chem. Ind. (London)*, 208 (1962).
39. E. C. Ashby, G. J. Brendel, H. E. Redman, *Inorg. Chem.*, **2**, 499 (1963).
40. T. N. Dymova, N. G. Eliseeva, S. I. Bakum, Yu. M. Dergachev, *Dokl. Akad. Nauk SSSR*, **215**, 1369 (1974).
41. E. C. Ashby, P. Kobetz, *Inorg. Chem.*, **5**, 1615 (1966).
42. E. Wiberg, T. Johannsen, *Die Chemie*, **55**, 38 (1942); *Chem. Abstr.*, **37**, 3363 (1943).
43. D. F. Shriver, R. W. Parry, N. N. Greenwood, A. Storr, M. G. H. Wallbridge, *Inorg. Chem.*, **2**, 867 (1963).
44. W. R. S. Garton, *Proc. Phys. Soc.*, **A64**, 509 (1951).

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Borides of Mn, Cr, Fe, Ni and Co also hydrolyze in aq HCl to afford borane mixtures composed primarily of B_2H_6 and B_4H_{10} ; however, the yields are low. The highest yield of borane available from these borides is 2% when Cr_2B is used⁷.

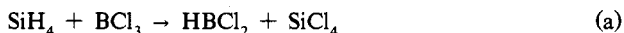
The hydrolysis of MgB_2 in strong base forms the tetrahydroborate anion⁸. Digestion of MgB_2 in 3M KOH or 4M $[(CH_3)_4N][OH]$ for 8–12 h followed by evaporation affords KBH_4 or $(CH_3)_4NBH_4$. Conversion of boron to $[BH_4]^-$ occurs to 10–15%.

(L. BARTON)

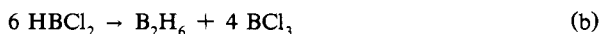
1. A. Stock, C. Massenez, *Chem. Ber.*, **45**, 3529 (1912).
2. R. Thompson, *Prog. Boron Chem.*, **2**, 176 (1970).
3. V. I. Mikeeva, V. Yu. Markina, *Zh. Neorg. Khim.*, **1**, 619 (1956).
4. R. C. Ray, P. C. Sinha, *J. Chem. Soc.*, 1694 (1935).
5. P. Duhart, *Ann. Chim. (Paris)*, **7**, 339 (1962).
6. P. L. Timms, C. S. G. Phillips, *Inorg. Chem.*, **3**, 297 (1964).
7. L. Ya. Markovskii, E. T. Bezruk, *J. Appl. Chem. USSR (Engl. Transl.)*, **35**, 491 (1962); *Chem. Abstr.*, **57**, 1853 (1962).
8. A. J. King, F. A. Kanda, V. A. Russell, W. J. Katz, *J. Am. Chem. Soc.*, **78**, 4176 (1956).

1.7.3.2. Involving the Reduction of Group IIIB Derivatives with Covalent Hydrides.

The reaction between SiH_4 and BCl_3 , which should yield diborane(6) according to bond energy calculations¹, occurs at 150°C to afford dichloroborane:

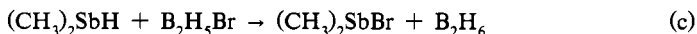


which subsequently disproportionates² to B_2H_6 :

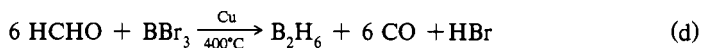


The same reaction proceeds at RT when catalyzed by methyl radicals to afford B_2H_6 in 67% yield¹. Similar conversions of B–halide bonds to B–H bonds are available from reactions of trichloroborane with disilane³ or alkylsilanes⁴.

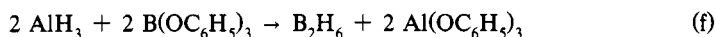
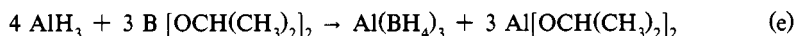
Dimethylstibine and 1-bromodiborane react⁵ rapidly at $-78^\circ C$:



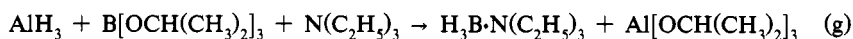
this reaction being favorable thermodynamically. At 400°C, haloboranes may be reduced⁶ to boranes by formaldehyde over activated Cu:



Borate esters are reduced by AlH_3 ; e.g., isopropylborate gives $Al(BH_4)_3$, whereas phenylborate gives B_2H_6 :



Reactions (e) and (f) are reversible. If the isopropylborate reaction is carried out in the presence of amine, the BH_3 amine adduct is formed:



130 1.7. Formation of Bonds between Hydrogen and B, Al, Ga, In, Tl
 1.7.3. from Group IIIB Derivatives

Borides of Mn, Cr, Fe, Ni and Co also hydrolyze in aq HCl to afford borane mixtures composed primarily of B₂H₆ and B₄H₁₀; however, the yields are low. The highest yield of borane available from these borides is 2% when Cr₂B is used⁷.

The hydrolysis of MgB₂ in strong base forms the tetrahydroborate anion⁸. Digestion of MgB₂ in 3M KOH or 4M [(CH₃)₄N][OH] for 8–12 h followed by evaporation affords KBH₄ or (CH₃)₄NBH₄. Conversion of boron to [BH₄][–] occurs to 10–15%.

(L. BARTON)

1. A. Stock, C. Massenez, *Chem. Ber.*, **45**, 3529 (1912).
2. R. Thompson, *Prog. Boron Chem.*, **2**, 176 (1970).
3. V. I. Mikeeva, V. Yu. Markina, *Zh. Neorg. Khim.*, **1**, 619 (1956).
4. R. C. Ray, P. C. Sinha, *J. Chem. Soc.*, 1694 (1935).
5. P. Duhart, *Ann. Chim. (Paris)*, **7**, 339 (1962).
6. P. L. Timms, C. S. G. Phillips, *Inorg. Chem.*, **3**, 297 (1964).
7. L. Ya. Markovskii, E. T. Bezruk, *J. Appl. Chem. USSR (Engl. Transl.)*, **35**, 491 (1962); *Chem. Abstr.*, **57**, 1853 (1962).
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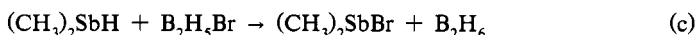


which subsequently disproportionates² to B₂H₆:

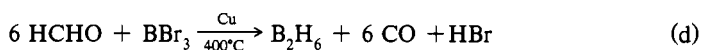


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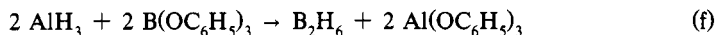
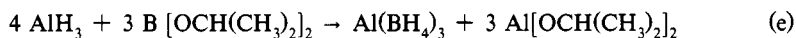
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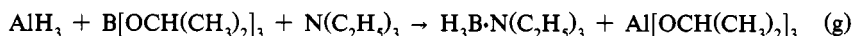
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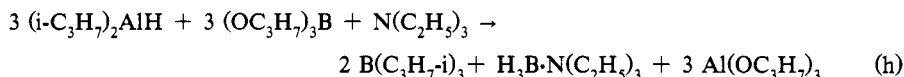
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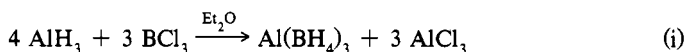
Reactions (e) and (f) are reversible. If the isopropylborate reaction is carried out in the presence of amine, the BH₃ amine adduct is formed:



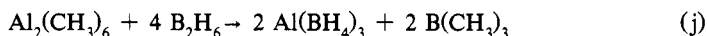
Alkylaluminum hydrides⁷ also reduce borate esters to BH_3 ; they function as mixtures of aluminum hydrides and aluminum alkyls, yielding both boranes and alkylborane:



The reaction between AlH_3 and BCl_3 affords B_2H_6 : however, because B_2H_6 reacts^{8,9} with further AlH_3 to give $\text{Al}(\text{BH}_4)_3$, the appropriate stoichiometry is:



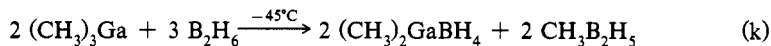
Reaction between $\text{Al}_2(\text{CH}_3)_6$ and xs B_2H_6 also produces $\text{Al}(\text{BH}_4)_3$.



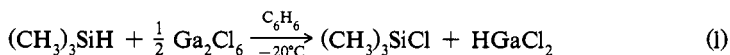
The species contains three $\text{Al} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array} \text{B}$ bridge bonds, which define a trigonal prism

about the Al atom¹¹. The analogous reaction between B_2H_6 and $\text{Ga}(\text{CH}_3)_3$ produces only the predicted decomposition products of $\text{Ga}(\text{BH}_4)_3$; however, at¹² -45°C ,

$(\text{CH}_3)_2\text{GaBH}_4$ containing two $\text{Ga} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{B} \end{array}$ bridge bonds¹³ is formed:

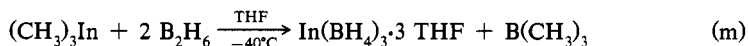


Treatment¹⁴ with $(\text{CH}_3)_3\text{SiH}$ in benzene or cyclohexane at $+20^\circ\text{C}$ reduces Ga_2Cl_6 to the HGaCl_2 :



The analogous reaction also occurs with Ga_2Br_6 .

The reaction between $\text{In}(\text{CH}_3)_3$ and B_2H_6 in tetrahydrofuran (THF) at -40°C affords the unstable $\text{In}(\text{BH}_4)_3 \cdot 3 \text{THF}$:



The species decomposes at -10°C to form B_2H_6 , In and H_2 . Because the structure is unknown, In—H bond formation is not confirmed¹⁵.

Polymeric $(\text{TiH})_x$ is prepared¹⁶ as a brown powder from TiOC_2H_5 and B_2H_6 in ether at -20°C .

(L. BARTON)

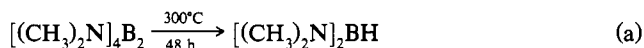
1. R. Schaeffer, L. Ross, *J. Am. Chem. Soc.*, **81**, 3486 (1959).
2. L. J. Edwards, R. K. Pearson, U.S. Pat. 3,007,768 (1957); cited in *Boron, Metalloborane Compounds and Boranes*, R. M. Adams, ed., Interscience, New York, 1964, p. 567.
3. C. H. Van Dyke, A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **25**, 1503 (1963).
4. H. Jenkner, Ger. Pat. 1,095,797 (1960); for source see ref. 2.
5. A. B. Burg, L. B. Grant, *J. Am. Chem. Soc.*, **81**, 1 (1959).
6. O. Glemser, Ger. Pat. 949,943 (1956); *Chem. Abstr.*, **51**, 14,785 (1957).
7. J. Kollonitsch, *Nature (London)*, **189**, 1005 (1961).
8. A. E. Finholt, A. C. Bond, H. I. Schelsinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

9. O. Stecher, E. Wiberg, *Chem. Ber.*, 75, 2003 (1942).
10. H. I. Schlesinger, R. T. Sanderson, A. B. Burg, *J. Am. Chem. Soc.*, 62, 3421 (1940).
11. A. Almenningen, G. Gunderson, A. Haaland, *Acta Chem. Scand.*, 22, 328 (1968).
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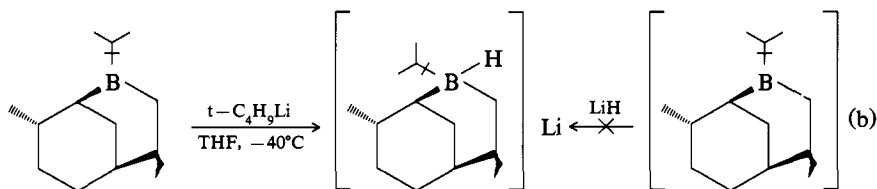
1.7.3.3. Involving Other Reactions.

Protonation of B—B bonds affords B— $\overset{\text{H}}{\diagup}$ B bridge bonds, and this is seen in the reaction of borane anions with protons¹. The reaction between B_6H_{10} and HBr and between $(\text{CO})_3\text{FeB}_5\text{H}_9$ and HBr both afford a B—H— μ bridge bond at a site where B—B (or Fe—B) bond existed. The hydride B_6H_{10} affords $[\text{B}_6\text{H}_{11}]^+$, and, when $(\text{CO})_3\text{FeB}_5\text{H}_9$ is protonated,³ the unique Fe—B bond is protonated to form $[(\text{CO})_3\text{FeB}_5\text{H}_{10}]^+$.

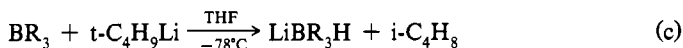
Pyrolysis of $[(\text{CH}_3)_2\text{N}]_4\text{B}_2$ at 300°C affords bis(dimethylamino)borane⁴:



As described in §1.7.4.1.4, ionic hydrides react with organoboranes to afford trialkylhydroborates. In some cases this reaction does not occur; however, treatment with $t\text{-C}_4\text{H}_9\text{Li}$ results in the formation of the desired compounds⁵:

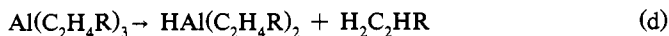


This reaction is general^{6,7}, with simple routes to trialkylhydroborates available. The method is effective for boranes from $\text{B}(\text{C}_2\text{H}_5)_3$ to such complex ones as phenyl-9-borabicyclo[3.3.1]nonane⁸. Reaction occurs when a slight xs of $(t\text{-C}_4\text{H}_9)\text{Li}$ in pentane is added dropwise to borane in THF at -78°C with vigorous stirring. The lithium trialkylhydroborate is formed quantitatively:



Use of CH_3Li produces only the so-called -ate complex.

Trialkylalanes decompose to form olefin and dialkylalane⁹:



This is a convenient laboratory synthesis of dialkylaluminum hydrides from trialkylalanes¹⁰, especially those with branched-chain alkyl groups. Diisobutylaluminum hydride is prepared by heating triisobutylalane under N_2 for 12 h at 160–180°C, followed

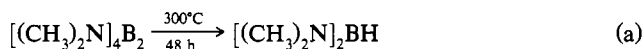
132 1.7. Formation of Bonds between Hydrogen and B, Al, Ga, In, Tl
 1.7.3. from Group IIIB Derivatives

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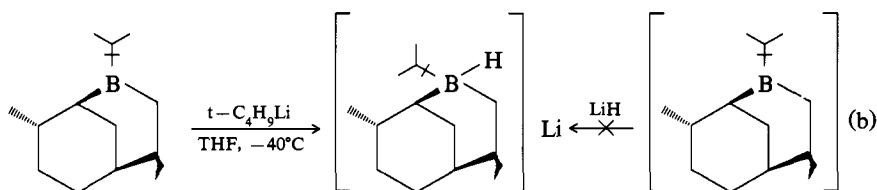
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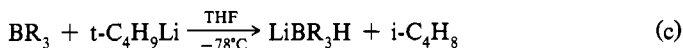
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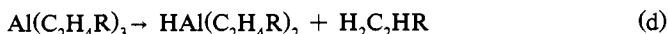


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Trialkylalanes decompose to form olefin and dialkylalane⁹:



This is a convenient laboratory synthesis of dialkylaluminum hydrides from trialkylalanes¹⁰, especially those with branched-chain alkyl groups. Diisobutylaluminum hydride is prepared by heating triisobutylalane under N_2 for 12 h at $160\text{--}180^\circ\text{C}$, followed

by fractional distillation. Yields are quantitative; about 60% of the trialkylalane is converted to the hydride, and the rest is recovered unreacted.

(L. BARTON)

1. R. J. Rummel, H. D. Johnson, I. S. Jaworinsky, S. G. Shore, *J. Am. Chem. Soc.*, **97**, 5395 (1975).
2. H. D. Johnson, V. T. Brice, G. L. Brubaker, S. G. Shore, *J. Am. Chem. Soc.*, **94**, 6711 (1972).
3. J. D. Ragaini, R. L. Smith, T. Schmitkons, M. Mangion, S. G. Shore, unpublished work.
4. R. J. Brotherton, L. L. Petterson, U.S. Pat. 3,006,730 (1962); *Chem. Abstr.*, **57**, 7105 (1962).
5. E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf, R. K. Varma, *J. Am. Chem. Soc.*, **93**, 1491 (1971).
6. E. J. Corey, R. K. Varma, *J. Am. Chem. Soc.*, **93**, 7319 (1971).
7. E. J. Corey, K. B. Becker, R. K. Varma, *J. Am. Chem. Soc.*, **94**, 8616 (1972).
8. H. C. Brown, G. W. Kramer, J. L. Hubbard, S. Krishnamurthy, *J. Organomet. Chem.*, **188**, 1 (1980).
9. K. Ziegler, H. G. Gellert, H. Lehmkuhl, W. Pfohl, K. Zosel, *Justus Liebigs Ann. Chem.*, **629**, 1 (1960).
10. J. J. Eisch, W. S. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966).

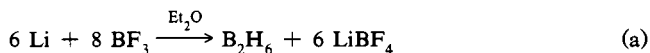
1.7.4. by Hydride Ion Reduction

1.7.4.1. of Compounds of Boron

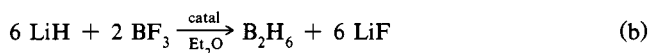
1.7.4.1.1. Involving Halides.

High yields of B—H compounds derive from reactions of metal hydrides with boron halides¹.

In the gas phase, LiH and BF₃ gas react only slightly at 180°C to give compounds containing B—H bonds. The reaction in Et₂O proceeds exothermically to afford B₂H₆ in two different stoichiometries^{2,3} at 250°C:



In the presence of traces of LiBH(OCH₃)₃ or B(OCH₃)₃ as catalysts:



The former reaction affords yields of 40% of diborane(6), whereas in the latter the yields are quantitative. The LiH + BCl₃ reaction proceeds as Eq. (b) without the catalyst.

These reaction mixtures may be used to form the tetrahydroborate ion; e.g., LiH and BF₃ react in nonethereal organic liquids to afford⁴ LiBH₄; LiBH₄ is available in 90% yield⁵ in the presence of B(OCH₃)₃ as catalyst via the intermediacy of B₂H₆, and similar yields arise from the reaction⁶ in an autoclave at 120°C.

In these reactions the effectiveness of the hydrides varies⁷ in the sequence LiH > NaH > KH; NaH reduces⁸ B halides to diborane(6). Reaction⁹ of xs BF₃ with NaH in glyme below 20°C affords B₂H₆ in 97% yields, but BCl₃ is not so effective¹⁰. However, BF₃ and NaH react at -70°C to form Na[HBf₃], which decomposes at 200°C. Also at 200°C in the presence of NaH, Na[H₂BF₂] is obtained from Na[HBf₃]. This method should be a convenient route to NaBH₄ but is not. Calcium hydride¹¹ reacts with BF₃·O(C₂H₅)₂ in O(C₂H₅)₂ at 120°C to afford B₂H₆.

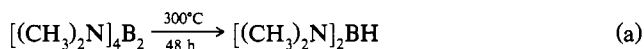
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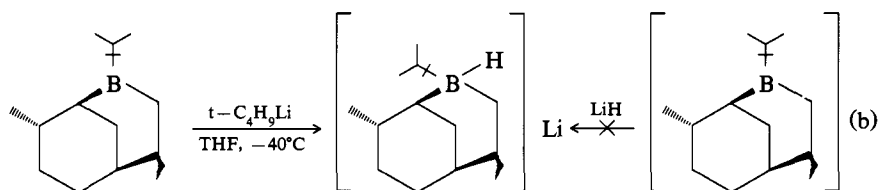
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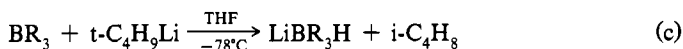
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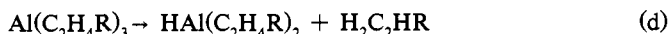


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Use of CH_3Li produces only the so-called -ate complex.

Trialkylalanes decompose to form olefin and dialkylalane⁹:



This is a convenient laboratory synthesis of dialkylaluminum hydrides from trialkylalanes¹⁰, especially those with branched-chain alkyl groups. Diisobutylaluminum hydride is prepared by heating triisobutylalane under N_2 for 12 h at $160\text{--}180^\circ\text{C}$, followed

by fractional distillation. Yields are quantitative; about 60% of the trialkylalane is converted to the hydride, and the rest is recovered unreacted.

(L. BARTON)

1. R. J. Rummel, H. D. Johnson, I. S. Jaworinsky, S. G. Shore, *J. Am. Chem. Soc.*, **97**, 5395 (1975).
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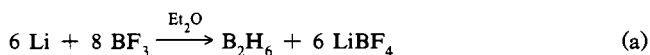
1.7.4. by Hydride Ion Reduction

1.7.4.1. of Compounds of Boron

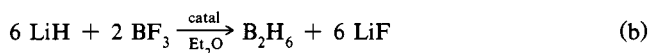
1.7.4.1.1. Involving Halides.

High yields of B—H compounds derive from reactions of metal hydrides with boron halides¹.

In the gas phase, LiH and BF₃ gas react only slightly at 180°C to give compounds containing B—H bonds. The reaction in Et₂O proceeds exothermically to afford B₂H₆ in two different stoichiometries^{2,3} at 250°C:



In the presence of traces of LiBH(OCH₃)₃ or B(OCH₃)₃ as catalysts:



The former reaction affords yields of 40% of diborane(6), whereas in the latter the yields are quantitative. The LiH + BCl₃ reaction proceeds as Eq. (b) without the catalyst.

These reaction mixtures may be used to form the tetrahydroborate ion; e.g., LiH and BF₃ react in nonethereal organic liquids to afford⁴ LiBH₄; LiBH₄ is available in 90% yield⁵ in the presence of B(OCH₃)₃ as catalyst via the intermediacy of B₂H₆, and similar yields arise from the reaction⁶ in an autoclave at 120°C.

In these reactions the effectiveness of the hydrides varies⁷ in the sequence LiH > NaH > KH; NaH reduces⁸ B halides to diborane(6). Reaction⁹ of xs BF₃ with NaH in glyme below 20°C affords B₂H₆ in 97% yields, but BCl₃ is not so effective¹⁰. However, BF₃ and NaH react at -70°C to form Na[HBf₃], which decomposes at 200°C. Also at 200°C in the presence of NaH, Na[H₂BF₂] is obtained from Na[HBf₃]. This method should be a convenient route to NaBH₄ but is not. Calcium hydride¹¹ reacts with BF₃·O(C₂H₅)₂ in O(C₂H₅)₂ at 120°C to afford B₂H₆.

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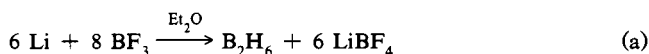
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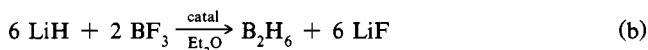
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The maximum yield^{12,13} of LiBH_4 from LiH and BF_3 in $(\text{C}_2\text{H}_5)_2\text{O}$ between -5 and 34°C are obtained at $3-10^\circ\text{C}$, and at $10-25^\circ\text{C}$ the major product is B_2H_6 .

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13. E. M. Fedneva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **4**, 286 (1959).

1.7.4.1.2. Involving Oxygen Compounds.

The reaction between borate esters and metal hydrides represents the most important development in borane chemistry, and the ultimate syntheses of tetrahydroborate salts have important consequences, especially in organic chemistry.

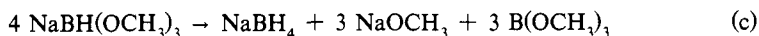
The presence of $\text{B}(\text{OCH}_3)_3$ has a solubilizing effect on LiH in ethers,¹ owing to^{2,3}:



This reaction is general and provides a convenient route to useful reducing agents. Sodium hydride reacts with $\text{B}(\text{OCH}_3)_3$ on refluxing for 5 h to afford $\text{NaBH}(\text{OCH}_3)_3$ in quantitative yield. In refluxing tetrahydrofuran (THF) the rate of reaction of NaH with borate esters decreases⁴ $\text{CH}_3 > \text{C}_2\text{H}_5 >>> \text{HC}(\text{CH}_3)_2 > \text{C}(\text{CH}_3)_3$. The time required for the isopropyl- and t-butylborates is reduced if glyme or diglyme is used as solvent at $130-150^\circ\text{C}$. The species formed are stable toward disproportionation and, therefore, are useful reducing reagents. Potassium hydride is more reactive⁵ toward borates than either LiH or NaH , e.g., triisopropylborate is nearly inert toward NaH at 20°C , requiring 83 h at reflux to react with xs hydride, but KH reacts completely in <1 h at 20°C :



Sodium trimethoxyhydroborate disproportionates at $250-250^\circ\text{C}$ to afford sodium tetrahydroborate:



However, this is not a good preparation of NaBH_4 because $\text{B}(\text{OCH}_3)_3$ must be removed continuously from the reaction medium and, furthermore, a competing process forming dimethoxyborane, $\text{HB}(\text{OCH}_3)_2$, occurs:



134 1.7. Formation of Bonds between Hydrogen and B, Al, Ga, In, Tl
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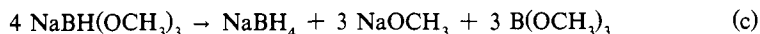
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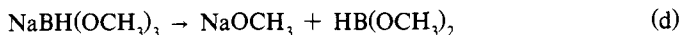
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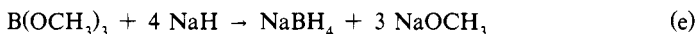
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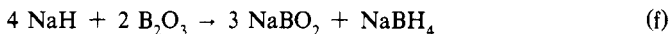


The most important reaction between hydrides and boron-oxygen compounds is⁶ between NaH and $\text{B}(\text{OCH}_3)_3$ to form NaBH_4 at 225–275°C:



Methylborate is added dropwise to NaH under N_2 at 230°C with vigorous stirring to form NaBH_4 in 90–96% purity and 94% yield. The $[\text{BH}_4]^-$ salt is extracted with liq NH_3 , filtered and the NH_3 boiled off. Recrystallization from H_2O or isopropylamine affords product in >99% yield. Reaction between NaH and $\text{NaBH}(\text{OCH}_3)_3$ at 250–260°C affords NaBH_4 in 78% yield. A reaction analogous to Eq. (e) produces LiBH_4 in 70% yield; however, extraction of the crude LiBH_4 from the mixture is difficult.

Boron(III) oxide may be reduced to the $[\text{BH}_4]^-$ ion by NaH under stringent conditions. Formation of NaBH_4 proceeds in 60% yield at 350°C while the reagents are ground together in a glass ball mill for 20–48 h:



Equation (e) is the most important reaction in which the B–H bond is formed because the product, NaBH_4 , is the starting material from which all other boranes are formed. The species is also a reagent in organic chemistry. The starting materials for Eq. (e) are readily available, and so this represents a convenient commercial route to B–H bonded compounds.

Other $\text{M}(\text{BH}_4)_x$ species may be prepared by extension of Eq. (e), e.g., $\text{Ca}(\text{BH}_4)_2$ is prepared by the reaction between CaH_2 and $\text{B}(\text{OCH}_3)_3$ in a pressure bomb⁷.

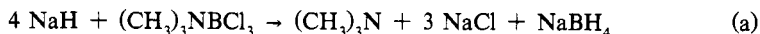
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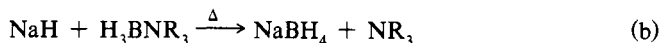
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Reduction of B–N to B–H bonds is difficult, and examples of this reaction are rare; e.g., $(\text{CH}_3)_2\text{NBCl}_2$ is reduced¹ only as far as $[(\text{CH}_3)_2\text{NBH}_2]$ and trichloroborazine is reduced only to the borazine², i.e., the B–N bonds in neither example react.

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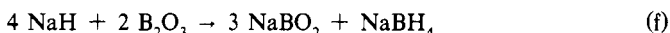
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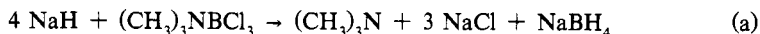
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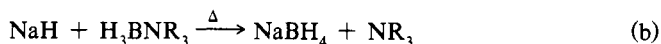
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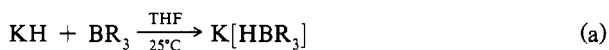


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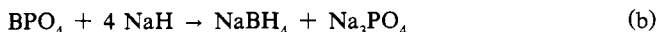
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Metal hydrides form addition compounds with triorganoboranes¹⁻⁴, which are useful reagents⁵; e.g., LiH and NaH react with triorganoboranes to afford the species Li [HBR₃]. However, long reaction times or reflux conditions are required, and with hindered triorganoboranes the reactions are slow⁶. On the other hand, KH reacts quantitatively with trialkyl or triarylboranes in tetrahydrofuran (THF) at 25°C:



Therefore, the species where R = C₂H₅, n-C₄H₉, sec-C₄H₉, C₃H₁₀, C₆H₁₂, exo-2-norbornyl, trans-2-methylcyclohexyl, 3-methyl-2-butyl and phenyl are conveniently prepared⁷⁻¹⁰. With the exception of K[HB(C₆H₅)₃], the reaction proceeds when THF and then triorganoborane is added to KH under Ar. Stirring for 1 h at 25°C effects 100% conversion to the triorganohydridoborate^{7,8}. In the preparation of K[HB(C₆H₅)₃] it is necessary to add B(C₆H₅)₃ in THF to KH in THF dropwise over 7 h. Additional stirring of the filtrate with [(C₂H₅)₄N]Br for 20 h followed by recrystallization affords [(C₂H₅)₄N][HB(C₆H₅)₃] in 56% yield¹⁰.

The B—P bond may be converted to B—H bonds, e.g.:



when the reaction is allowed to proceed in mineral oil at 288–300°C for 2 h¹¹.

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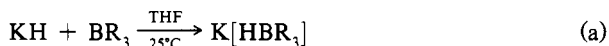
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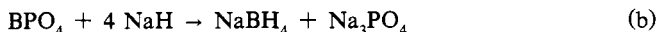
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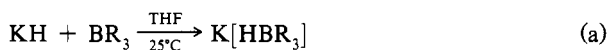
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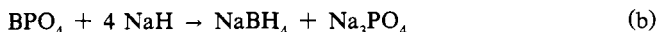
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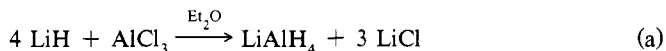
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1.7. Formation of Bonds between Hydrogen and B, Al, Ga, In, Tl 137

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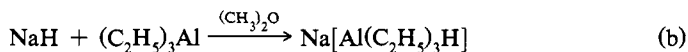
precipitated LiCl and xs LiH is effected by filtration and LiAlH_4 is obtained in > 95% yields:



The LiAlH_4 used as promotor is obtained by reaction between LiH and AlCl_3 in dioxane or ether. This process affords LiAlH_4 in low yields ($\sim 30\%$), and the reaction mixture requires heating to 50°C in dioxane or periodic cooling with liq N_2 when ether is the solvent.

Improvements in this process to eliminate the necessity for finely grinding the LiH or using LiAlH_4 as promotor² have only limited success. The reaction may be initiated by the addition³ of I_2 , and the substitution⁴ of AlBr_3 for AlCl_3 eliminates the need to grind the LiH; however, this results in product contaminated with AlBr_3 because the latter is soluble in diethyl ether. Optimization of the conditions for Eq. (a) involves the intermediates⁵ AlH_3 and $\text{AlH}_3\text{AlCl}_3$; optimum conditions are $0-4^\circ\text{C}$ when an induction period is not necessary⁶, and a slow rate of addition of AlCl_3 , which reduces the formation of Cl-containing alanes⁷. An alternative procedure⁸ for the preparation of LiAlH_4 employs LiH and AlBr_3 in the solvent system $\text{C}_6\text{H}_6-(\text{C}_2\text{H}_5)_2\text{O}$.

Preparation⁹ of NaAlH_4 in 60% yield results from NaH and AlBr_3 in $(\text{CH}_3)_2\text{O}$. The reaction between NaH and AlCl_3 in $(\text{C}_2\text{H}_5)_2\text{O}$ does not proceed well owing to the limited solubility of NaH; however, the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$ as catalyst solubilizes the NaH as $\text{Na}[\text{Al}(\text{C}_2\text{H}_5)_3\text{H}]$ and facilitates the reaction¹⁰:



Reaction between KH and AlCl_3 produces $\text{K}[\text{AlH}_4]$ in the solvents $\text{C}_6\text{H}_6-(\text{C}_2\text{H}_5)_2\text{O}$ when $\text{Al}(\text{C}_2\text{H}_5)_3$ or $(i\text{-C}_4\text{H}_9)_2\text{AlH}$ is present as catalyst¹⁰.

Dialkylaluminum hydrides, important reagents industrially, are prepared by treatment¹¹ of dialkylaluminum halides with LiH, e.g., diisobutylaluminum hydride (or deuteride) may be prepared by treatment of $(i\text{-C}_4\text{H}_9)_2\text{AlCl}$ with LiH in ether^{12,13}; LiH or LiD in ether is cooled to 0°C and $(i\text{-C}_4\text{H}_9)_2\text{AlCl}$ is added dropwise under N_2 so that an xs of LiH exists. The mixture is heated to reflux for 48 h or until a Cl^- test shows negative. After workup $(i\text{-C}_4\text{H}_9)_2\text{AlH}$ is obtained in 67% yield.

The species $\text{C}_2\text{H}_5\text{OAlCl}_2$ may be converted to the salt $\text{Na}[\text{AlH}_3\text{OC}_2\text{H}_5]$ by treatment¹⁴ with NaH in tetrahydrofuran (THF). The $\text{C}_2\text{H}_5\text{OAlCl}_2$ in THF is added dropwise to NaH and the resulting mixture stirred and maintained at 40°C for 20 min by external cooling with solid CO_2 . The resulting $\text{Na}[\text{AlH}_3\text{OC}_2\text{H}_5]$ is obtained in 68% yield.

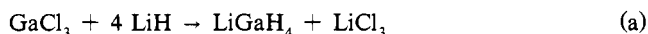
(L. BARTON)

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2. E. C. Ashby, *Adv. Inorg. Chem. Radiochem.*, **8**, 283 (1966).
3. E. Wiberg, *Z. Naturforsch., Teil B*, **6**, 393 (1951).
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5. V. I. Mikheeva, E. M. Fedneva, Z. L. Shnitkova, *Zh. Neorg. Khim.*, **1**, 2440 (1956).
6. V. I. Mikheeva, M. S. Selivokhina, V. V. Leonova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **4**, 2436 (1959).

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1.7.4.3. of Compounds of Gallium.

Anhydrous GaCl_3 reacts with a fourfold xs of finely ground LiH in ether when the reaction mixture is slowly warmed from -80°C to 25°C . The white, solid product is isolated in 76% yield after filtration and removal of solvent in vacuo¹:



The reaction can be carried out² at 0°C , and, if the reaction mixture is warmed to 35°C while $\text{N}(\text{CH}_3)_3$ is added, a 95% yield is obtained³.

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1.7.4.4. of Compounds of Indium.

Treatment of InCl_3 or InBr_3 with an equimolar quantity of finely divided LiH in ether at -25°C affords LiInH_4 in 60–65% or 80% yield, respectively. When LiH reacts with InCl_3 in refluxing $(\text{C}_2\text{H}_5)_2\text{O}$, $(\text{InH}_3)_x$ and LiCl are formed¹. When In trihalides react with large granules of LiH , the trihaloindo hydrides are formed², e.g., LiH and InBr_3 in ether at 0°C afford $\text{LiInBr}_3\text{H} \cdot 6 \text{O}(\text{C}_2\text{H}_5)_2$ in 40% yield and LiH and InI_3 afford the corresponding species $\text{LiInI}_3\text{H} \cdot 6 \text{O}(\text{C}_2\text{H}_5)_2$ under the same conditions.

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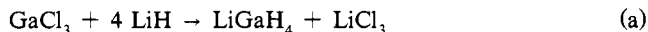
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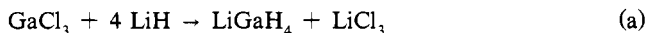
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14. G. Hamprecht, M. Schwarzmann, M. Tittel, Ger. Pat. 1,085,515 (1960); *Chem. Abstr.*, **55**, 15,350 (1961).

1.7.4.3. of Compounds of Gallium.

Anhydrous GaCl_3 reacts with a fourfold xs of finely ground LiH in ether when the reaction mixture is slowly warmed from -80°C to 25°C . The white, solid product is isolated in 76% yield after filtration and removal of solvent in vacuo¹:



The reaction can be carried out² at 0°C , and, if the reaction mixture is warmed to 35°C while $\text{N}(\text{CH}_3)_3$ is added, a 95% yield is obtained³.

(L. BARTON)

1. A. E. Finholt, A. C. Bond, H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).
2. N. N. Greenwood, A. Storr, M. G. H. Wallbridge, *Inorg. Chem.*, **2**, 1036 (1963).
3. E. Wiberg, M. Schmidt, *Z. Naturforsch., Teil B*, **6**, 171 (1951).

1.7.4.4. of Compounds of Indium.

Treatment of InCl_3 or InBr_3 with an equimolar quantity of finely divided LiH in ether at -25°C affords LiInH_4 in 60–65% or 80% yield, respectively. When LiH reacts with InCl_3 in refluxing $(\text{C}_2\text{H}_5)_2\text{O}$, $(\text{InH}_3)_x$ and LiCl are formed¹. When In trihalides react with large granules of LiH , the trihaloindo hydrides are formed², e.g., LiH and InBr_3 in ether at 0°C afford $\text{LiInBr}_3\text{H}\cdot 6 \text{O}(\text{C}_2\text{H}_5)_2$ in 40% yield and LiH and InI_3 afford the corresponding species $\text{LiInI}_3\text{H}\cdot 6 \text{O}(\text{C}_2\text{H}_5)_2$ under the same conditions.

(L. BARTON)

1. E. Wiberg, M. Schmidt, *Z. Naturforsch., Teil B*, **12**, 54 (1957).
2. E. Wiberg, O. Dittmann, H. Nöth, M. Schmidt, *Z. Naturforsch., Teil B*, **12**, 56 (1957).

1.7.4.5. of Compounds of Thallium.

Treatment of TlCl_3 with pure, finely divided LiH in $(\text{C}_2\text{H}_5)_2\text{O}$ at -15°C affords LiTiH_4 . At higher T the LiTiH_4 cannot be isolated.

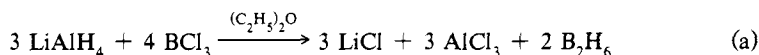
(L. BARTON)

1. E. Wiberg, O. Dittmann, M. Schmidt, *Z. Naturforsch., Teil B*, **12**, 60 (1957).

1.7.5. from Complex Hydrides

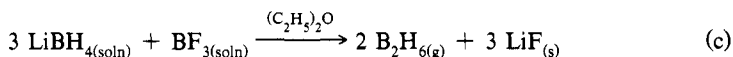
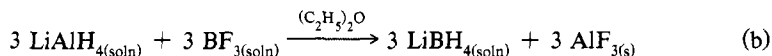
1.7.5.1. with Compounds of Boron.

The reaction between BCl_3 and LiAlH_4 in ether affords B_2H_6 quantitatively¹:

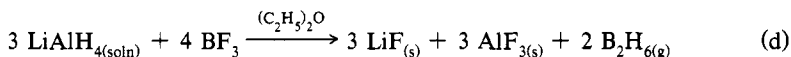


An xs of BCl_3 is distilled into the LiAlH_4 in $(\text{C}_2\text{H}_5)_2\text{O}$ at -196°C . The mixture is warmed to 25°C and thoroughly mixed, the B_2H_6 distills through a trap maintained at -112°C and the xs BCl_3 forms a complex with the solvent. Because LiAlH_4 may be prepared simply from LiH and AlCl_3 , the process may be considered as a synthesis from LiH and BCl_3 with AlCl_3 present as a solubilizing agent for LiH .

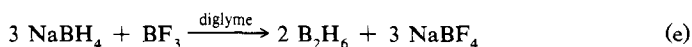
The reaction^{2,3} between LiAlH_4 and BF_3 proceeds in two well-defined steps:



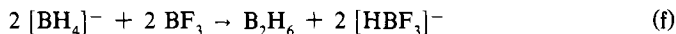
Overall:



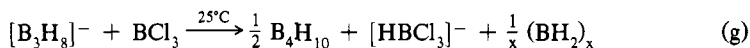
Other methods involving halide-hydride exchange starting with $[\text{BH}_4]^-$ ion are available^{4,5}. These are included here because formation of BHB bridge bonds from B—H terminal bonds is interpreted as new B—H bond formation, e.g., BF_3 and NaBH_4 react⁶ in diglyme to afford B_2H_6 in yields $>90\%$:



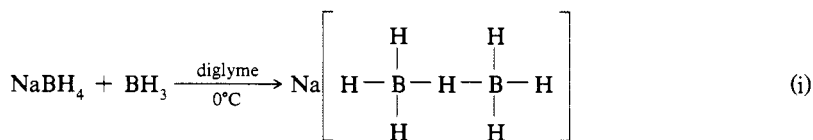
Hydride abstraction from tetrahydroborate anions is the most convenient route for the preparation of boranes^{7,8}. In these processes an unstable intermediate transfers a BH_3 moiety and in so doing forms new BHB bridge bonds. The simplest of these reactions involves the formation of B_2H_6 from NaBH_4 and BF_3 at 25°C . In addition to forming new B—H—B bonds in B_2H_6 , 1 mol of $[\text{HBF}_3]^-$ is formed per mol of $[\text{BH}_4]^-$:



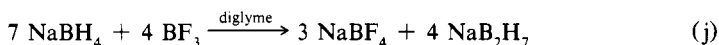
This process also occurs for higher boranes, e.g.:



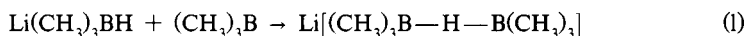
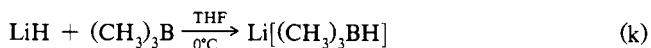
New BHB bridge bonds form from terminal B—H bonds; e.g., LiBH_4 and NaBH_4 absorb 1 mol equiv of borane^{6,9-11}:



The same product is formed⁶ from the reaction of NaBH_4 with diborane formed in situ from BF_3 and NaBH_4 :

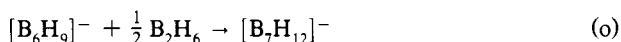
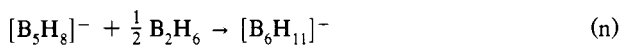
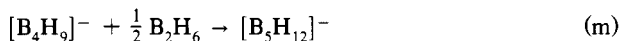


This reaction¹² does not occur with KBH_4 . Similar hexaalkyldiborohydrides are available when LiH is treated with 2 equiv of trialkylborane in tetrahydrofuran (THF), glyme or diglyme¹³:

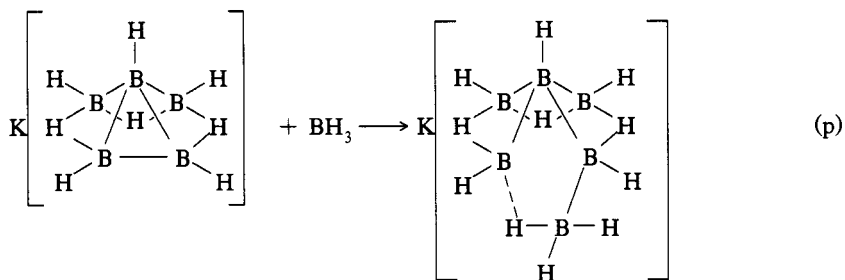


When such solvents as $(\text{C}_2\text{H}_5)_2\text{O}$ or $(\text{n-C}_4\text{H}_9)_2\text{O}$, which are poor solvating media for the Li^+ ion, are used, the second mol of alkylborane does not add to the $[(\text{CH}_3)_3\text{BH}]^-$ ion, which must be strongly associated with the Li^+ ion.

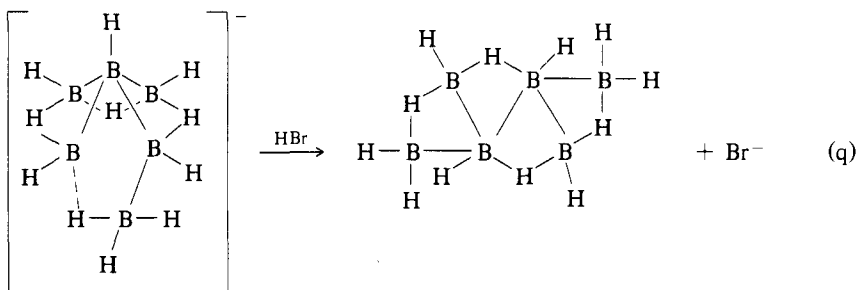
Other examples of new $\text{B}-\text{H}-\text{B}$ bridge formation involve the condensation of hydroborate anions with neutral boranes to form large boranes or borane anions. Borane will add to the anions $[\text{B}_4\text{H}_9]^-$, $[\text{B}_5\text{H}_8]^-$, and $[\text{B}_6\text{H}_9]^-$ to form the species $[\text{B}_5\text{H}_{12}]^-$, $[\text{B}_6\text{H}_{11}]^-$ and $[\text{B}_7\text{H}_{12}]^-$, respectively¹⁴:



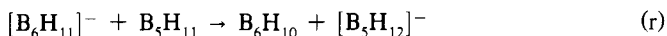
These reactions proceed at -78°C in ethers by the addition of a BH_3 group to a $\text{B}-\text{B}$ bond in the anion. The products are fluxional, bridging hydrogens moving into and out of vacant $\text{B}-\text{B}$ bond sites in solution. New $\text{B}-\text{H}$ bonds are formed:



The protonation of borane anions affords new $\text{B}-\text{H}$ bonds; e.g., protonation¹⁴ of $[\text{B}_6\text{H}_{11}]^-$ formed in Eq. (p) affords B_6H_{12} :

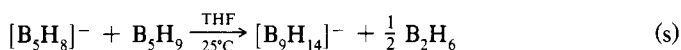


This is not always the case, for when H^+ is added to $[\text{B}_5\text{H}_{12}]^-$, H_2 is eliminated and B_5H_{11} is formed¹⁴. Hydride transfer between boranes and hydroborate anions can occur:



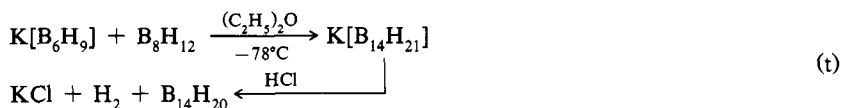
These polyhedral expansion reactions of boranes have synthetic utility.

The decomposition of $[\text{B}_5\text{H}_8]^-$ proceeds via the formation¹⁵⁻¹⁷ of $[\text{B}_9\text{H}_{14}]^-$ in the presence of B_5H_9 :

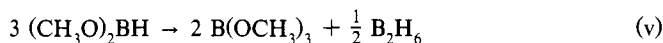
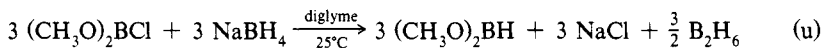


Although the stoichiometry is not as simple as indicated in Eq. (s), the reaction proceeds^{7,8} when 2 mol B_5H_9 are treated with 1 mol NaH in THF at 25°C .

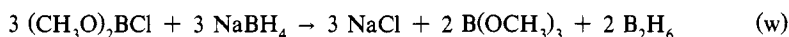
Insertion of boron atoms from larger boranes into the B—B bonds of higher tetrahydroborate anions proceeds with the formation of new B—H bonds and represents a rational approach to the synthesis of higher boranes, e.g., B_8H_{12} combines¹⁸ with $[\text{B}_6\text{H}_9]^-$ at -78°C to form $[\text{B}_{14}\text{H}_{21}]^-$. Protonation of the latter affords $\text{B}_{14}\text{H}_{20}$:



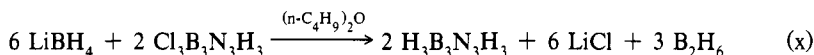
Bonds B—O or B—N are not reduced by reaction with complex hydrides, and so selective reductions are possible. Treatment of $(\text{CH}_3\text{O})_2\text{BCl}$ with NaBH_4 in diglyme affords¹⁹ B_2H_6 , via the intermediacy of $\text{HB}(\text{OCH}_3)_2$:



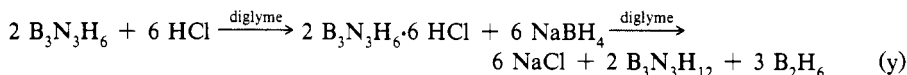
Overall:



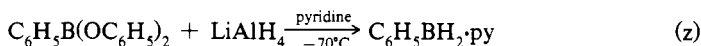
Similarly, B-trichloroborazine is reduced^{19,20} to $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$ at 25°C by treatment with LiBH_4 in $(n\text{-C}_4\text{H}_9)_2\text{O}$:



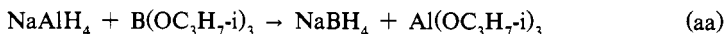
Moreover, $B_3N_3H_6$ may be reduced to $B_3N_3H_{12}$ by treatment with HCl to form the hydrochloride followed by reaction with $NaBH_4$ in diglyme²¹:



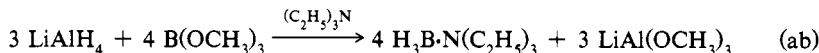
Boranes may be prepared by reduction of B—O bonds using $LiAlH_4$, e.g., $C_6H_5 \cdot B(OC_6H_5)_2$ or $(C_6H_5BO)_3$ reacts with $LiAlH_4$ in $(C_2H_5)_2O$ containing xs C_5H_5N at 70°C to form the air-stable pyridine—borane²²:



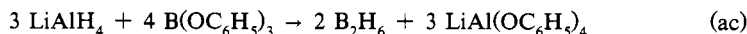
Other pyridine boranes, $RBH_2 \cdot C_5H_5N$, are prepared, where $R = p\text{-ClC}_6\text{H}_4$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$, $\alpha\text{-C}_{10}\text{H}_7$, $1\text{-C}_3\text{H}_7$, $1\text{-C}_4\text{H}_9$; $R_2BH \cdot NC_5H_5$ also, can be prepared, where $R = C_6H_5$, $p\text{-ClC}_6\text{H}_4$, $p\text{-CH}_3\text{C}_6\text{H}_4$ or $p\text{-CH}_3\text{OC}_6\text{H}_4$. Trialkylborates may be reduced to B_2H_6 by treatment with MBH_4 or $MAIH_4$ in ethers or in the absence of solvent²³:



This reaction may be general for all lower alkylborates; e.g., treatment of $B(OCH_3)_3$ with $LiAlH_4$ affords a mixture not easily identified. Addition of $LiAlH_4$ to $B(OCH_3)_3$ in $(C_2H_5)_2O$ forms $LiBH_4$ and LiB_2H_7 among the products; however, in $(C_2H_5)_3N$ as solvent, the borane adduct is formed²⁴:



When triphenylborate is used, $LiAlH_4$ forms $LiBH_4$ if the borate ester is added to the $LiAlH_4$ solution. If $LiAlH_4$ is added to $B(OC_6H_5)_3$, B_2H_6 is formed:



In this reaction only 43% yield of B_2H_6 forms owing to a side reaction in which AlH_3 is formed, so $LiAlH_4$ is more reactive²⁴ toward B—OR compounds than $NaBH_4$.

Circulation of $B_2H_{6(g)}$ over solid $LiAlH_4$ at 80—90°C affords $Al(BH_4)_3$ in 90% yield.¹ The $Al(BH_4)_3$ is collected at -80°C in a U-trap:



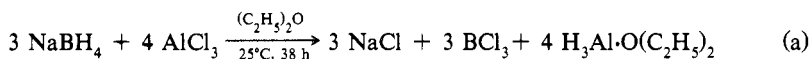
(L. BARTON)

1. A. E. Finholt, A. C. Bond, H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).
2. R. C. Lord, E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).
3. I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnich, G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).
4. R. M. Adams, ed., *Boron, Metalloboron Compounds and Boranes*, Interscience, New York, 1964, Ch. 7.
5. R. W. Parry, M. K. Walter, *Prep. Inorg. React.*, **5**, 46 (1968).
6. H. C. Brown, P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).
7. J. B. Leach, M. A. Toft, F. L. Himpsl, S. G. Shore, *J. Am. Chem. Soc.*, **103**, 988 (1981).
8. M. A. Toft, J. B. Leach, F. L. Himpsl, S. G. Shore, *Inorg. Chem.*, **21**, 1952 (1982).
9. H. C. Brown, P. F. Stehle, P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).
10. W. G. Evans, C. E. Holloway, K. Sukumarabandhu, D. H. McDaniel, *Inorg. Chem.*, **7**, 1746 (1968).
11. R. K. Hertz, H. D. Johnson II, S. G. Shore, *Inorg. Synth.*, **17**, 24 (1977).

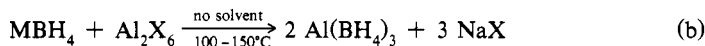
12. K. R. Pearson, L. L. Lewis, L. J. Edwards, *Reaction of Potassium Borohydride with Boron Trifluoride*, P. M. Maginnity, ed., Project ZIP, Contract No. a(s)-S2-1024-C (1957); *Nucl. Sci. Abstr.*, 12, 4069 (1958).
13. H. C. Brown, A. Khuri, S. Krishnamurthy, *J. Am. Chem. Soc.*, 99, 6237 (1977).
14. R. J. Remmel, H. D. Johnson II, I. S. Jaworowsky, S. G. Shore, *J. Am. Chem. Soc.*, 97, 5395 (1975).
15. V. T. Brice, H. D. Johnson, II, D. L. Denton, S. G. Shore, *Inorg. Chem.*, 11, 1135 (1972).
16. C. G. Savory, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 179 (1974).
17. L. Barton, T. Onak, S. G. Shore, *Gmelin Handbuch der Anorganischen Chemie*, Springer-Verlag, Berlin, 1979, Vol. 54, Ch. 4, p. 113.
18. J. C. Huffman, D. C. Moody, R. Schaeffer, *J. Am. Chem. Soc.*, 97, 1621 (1974).
19. H. Nöth, *Angew. Chem.*, 73, 371 (1961).
20. R. Schaeffer, M. Steindler, L. Holnstedt, H. S. Smith, L. B. Eddy, H. I. Schlesinger, *J. Am. Chem. Soc.*, 76, 3303 (1954).
21. G. H. Dahl, R. Schaeffer, *J. Am. Chem. Soc.*, 83, 3032 (1961).
22. M. F. Hawthorne, *Chem. Ind. (London)*, 1242 (1957).
23. J. Kollonitsch, *Nature (London)*, 189, 1005 (1961).
24. E. C. Ashby, *Adv. Inorg. Chem. Radiochem.*, 8, 283 (1966).

1.7.5.2. with Compounds of Aluminum, Gallium, Indium and Thallium.

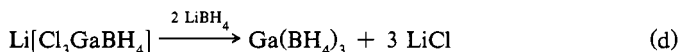
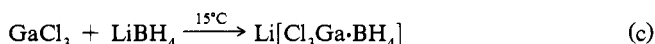
Treatment of AlCl_3 with NaBH_4 at 25°C in ether for 38 h affords¹ $\text{H}_3\text{Al}\cdot\text{O}(\text{C}_2\text{H}_5)_2$:



In the absence of solvent at $100\text{--}150^\circ\text{C}$, MBH_4 salts and Al halides afford² $\text{Al}(\text{BH}_4)_3$. The reaction proceeds for $\text{X} = \text{Cl}, \text{Br}$, and the reactivities of the MBH_4 salts decrease $\text{Li} > \text{Na} > \text{K}$.

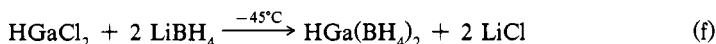
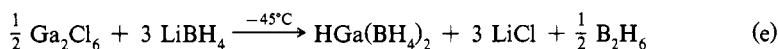


The tetrahydroborates of Ga are well established, although $\text{Ga}(\text{BH}_4)_3$ is unstable, and only its decomposition products are isolable³:



Species containing the BH_4 moiety and other atoms covalently bound to Ga are more stable, and their structures contain the Ga $\begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{Ga} \quad \text{B} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$ moiety⁴.

Such species are available from reactions at low T, e.g., either powdered Ga_2Cl_6 or HGaCl_2 affords $\text{HGa}(\text{BH}_4)_2$ with xs LiBH_4 at -45°C in the absence of solvent⁵:



The mixed species $(\text{CH}_3)_2\text{GaCl}$ and $(\text{CH}_3)_3\text{N}\cdot\text{GaH}_2\text{Cl}$, prepared from exchange reactions, are converted to the corresponding borohydrides by treatment with LiBH_4 at low T, e.g., $(\text{CH}_3)_2\text{GaBH}_4$ is prepared⁶ in the absence of solvent at -15°C and $(\text{CH}_3)_3\text{N}\cdot\text{GaH}_2(\text{BH}_4)$ with xs LiBH_4 at low T in benzene or ether⁷:

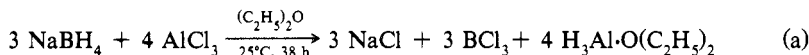
1.7. Formation of Bonds between Hydrogen and B, Al, Ga, In, Tl 143

1.7.5. from Complex Hydrides

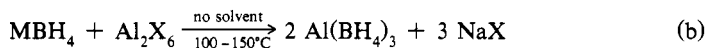
12. K. R. Pearson, L. L. Lewis, L. J. Edwards, *Reaction of Potassium Borohydride with Boron Trifluoride*, P. M. Maginnity, ed., Project ZIP, Contract No. a(s)-S2-1024-C (1957); *Nucl. Sci. Abstr.*, 12, 4069 (1958).
13. H. C. Brown, A. Khuri, S. Krishnamurthy, *J. Am. Chem. Soc.*, 99, 6237 (1977).
14. R. J. Rimmel, H. D. Johnson II, I. S. Jaworowsky, S. G. Shore, *J. Am. Chem. Soc.*, 97, 5395 (1975).
15. V. T. Brice, H. D. Johnson, II, D. L. Denton, S. G. Shore, *Inorg. Chem.*, 11, 1135 (1972).
16. C. G. Savory, M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 179 (1974).
17. L. Barton, T. Onak, S. G. Shore, *Gmelin Handbuch der Anorganischen Chemie*, Springer-Verlag, Berlin, 1979, Vol. 54, Ch. 4, p. 113.
18. J. C. Huffman, D. C. Moody, R. Schaeffer, *J. Am. Chem. Soc.*, 97, 1621 (1974).
19. H. Nöth, *Angew. Chem.*, 73, 371 (1961).
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21. G. H. Dahl, R. Schaeffer, *J. Am. Chem. Soc.*, 83, 3032 (1961).
22. M. F. Hawthorne, *Chem. Ind. (London)*, 1242 (1957).
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24. E. C. Ashby, *Adv. Inorg. Chem. Radiochem.*, 8, 283 (1966).

1.7.5.2. with Compounds of Aluminum, Gallium, Indium and Thallium.

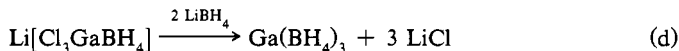
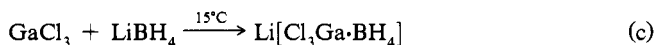
Treatment of AlCl_3 with NaBH_4 at 25°C in ether for 38 h affords¹ $\text{H}_3\text{Al}\cdot\text{O}(\text{C}_2\text{H}_5)_2$:



In the absence of solvent at $100\text{--}150^\circ\text{C}$, MBH_4 salts and Al halides afford² $\text{Al}(\text{BH}_4)_3$. The reaction proceeds for $\text{X} = \text{Cl}, \text{Br}$, and the reactivities of the MBH_4 salts decrease $\text{Li} > \text{Na} > \text{K}$.

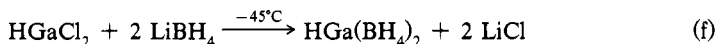
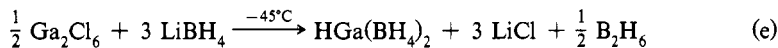


The tetrahydroborates of Ga are well established, although $\text{Ga}(\text{BH}_4)_3$ is unstable, and only its decomposition products are isolable³:

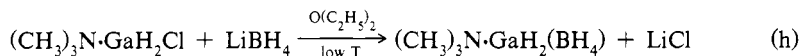
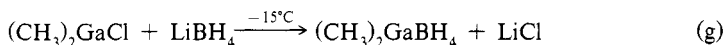


Species containing the BH_4 moiety and other atoms covalently bound to Ga are more stable, and their structures contain the $\text{Ga} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array} \text{B} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$ moiety⁴.

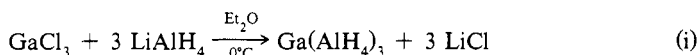
Such species are available from reactions at low T, e.g., either powdered Ga_2Cl_6 or HGaCl_2 affords $\text{HGa}(\text{BH}_4)_2$ with xs LiBH_4 at -45°C in the absence of solvent⁵:



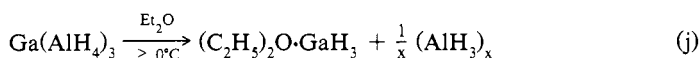
The mixed species $(\text{CH}_3)_2\text{GaCl}$ and $(\text{CH}_3)_3\text{N}\cdot\text{GaH}_2\text{Cl}$, prepared from exchange reactions, are converted to the corresponding borohydrides by treatment with LiBH_4 at low T, e.g., $(\text{CH}_3)_2\text{GaBH}_4$ is prepared⁶ in the absence of solvent at -15°C and $(\text{CH}_3)_3\text{N}\cdot\text{GaH}_2(\text{BH}_4)$ with xs LiBH_4 at low T in benzene or ether⁷:



The unstable $\text{Ga}(\text{AlH}_4)_3$, which contains the $\text{Ga} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array} \text{Al} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$ moiety, is available from the reaction⁸ between GaCl_3 and LiAlH_4 in ether at 0°C .

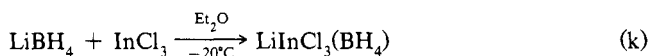


The $\text{Ga}(\text{AlH}_4)_3$ decomposes to $\text{H}_3\text{Ga}\cdot\text{O}(\text{C}_2\text{H}_5)_2$ and $(\text{AlH}_3)_x$ in ether above 0°C :



Above 35°C , GaH_3 itself decomposes to the elements.

Compounds containing $\text{In}-\text{H}$ bonds may also be prepared from InX_3 ($\text{X} = \text{Cl}, \text{Br}$) and complex hydrides, e.g., at -20°C InCl_3 reacts⁹ with LiBH_4 in ether to form $\text{LiInCl}_3(\text{BH}_4)$:



The structure of $\text{LiInCl}_3(\text{BH}_4)$ is unknown. It is stable at -40°C but at -20°C loses BH_3 to afford LiInCl_3H . Similar reactions occur with InBr_3 . The LiInX_3H species are $\text{LiX}\cdot\text{InX}_3\text{H}$ in ethers, and in the absence of ether, $\text{LiH}\cdot\text{InX}_3$.

Ethereal InCl_3 reacts with LiAlH_4 at -70°C to afford¹⁰ $\text{In}(\text{AlH}_4)_3$:



The $\text{In}(\text{AlH}_4)_3$ decomposes above -40°C , to form AlH_3 , In and H_2 via the intermediacy of InH_3 . When InCl_3 is treated at 25°C with $1/3$ equiv of LiAlH_4 , $\text{LiInCl}_3(\text{AlH}_4)$ is obtained, which is stable $\leq 100^\circ\text{C}$. The ether insolubility of $\text{In}(\text{AlH}_4)_3$ and $\text{InCl}_2\cdot$

(AlH_4) suggests that these species do not contain $\text{In} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{Al} \end{array}$ bonds.

The $\text{Tl}-\text{H}$ bond may be formed by decomposition of TlBH_4 . Treatment of TlOC_2H_5 with LiBH_4 in ether affords¹¹ TlBH_4 . This species is ionic and so does not contain $\text{Tl}-\text{H}$ bonds¹²; however, at $\geq 40^\circ\text{C}$, TlBH_4 decomposes to B_2H_6 and TlH , and TlCl_3 is reduced to TiCl on treatment with LiBH_4 . If the reaction is carried out at -100°C , an unstable intermediate of unknown structure, $\text{TlCl}(\text{BH}_4)_2$, forms, which decomposes above -95°C .

A species^{13,14} of unknown structure, $\text{Tl}(\text{GaH}_4)_3$, which decomposes above -90°C , may be prepared from TlCl_3 and LiGaH_4 in ether at -115°C .

(L. BARTON)

1. S. G. Shore, R. W. Parry, *J. Am. Chem. Soc.*, **80**, 12 (1958).
2. H. I. Schlesinger, H. C. Brown, E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 209 (1953).
3. E. Wiberg, O. Dittman, H. Nöth, M. Schmidt, *Z. Naturforsch., Teil B*, **12**, 56 (1957).
4. M. T. Barlow, A. J. Downs, P. D. P. Thomas, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1793 (1979).

5. A. J. Downs, P. D. P. Thomas, *J. Chem. Soc., Chem. Commun.*, 825 (1976).
6. A. J. Downs, P. D. P. Thomas, *J. Chem. Soc., Dalton Trans.*, 809 (1978).
7. N. N. Greenwood, A. Storr, *J. Chem. Soc.*, 3420 (1965).
8. E. Wiberg, M. Schmidt, *Z. Naturforsch., Teil B*, 6, 171 (1951).
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10. E. Wiberg, M. Schmidt, *Z. Naturforsch., Teil B*, 6, 172 (1951).
11. E. Wiberg, O. Dittman, H. Nöth, M. Schmidt, *Z. Naturforsch., Teil B*, 12, 62 (1957).
12. T. C. Waddington, *J. Chem. Soc.*, 4783 (1958).
13. E. Wiberg, H. Noth, *Z. Naturforsch., Teil B*, 12, 6, 63 (1957).
14. E. Wiberg, M. Schmidt, *Z. Naturforsch., Teil B*, 355 (1951).

1.7.6. by Industrial Processes.

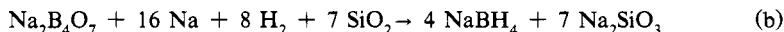
The important industrial chemicals containing group III element-hydrogen bonds are NaBH_4 and LiAlH_4 because all industrial products containing such bonds are derived from these two chemicals.

In the U.S., NaBH_4 is prepared¹ commercially from NaH and $\text{B}(\text{OCH}_3)_3$ in high-bp mineral oil at ca. 275°C:



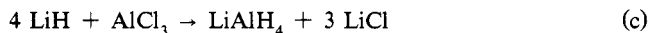
The NaH is prepared on site in the NaBH_4 production plant, and an oil slurry is fed into a mixing tank into which $\text{B}(\text{OCH}_3)_3$ also flows. The product slurry is added to H_2O , the aq layer is separated from the oil, and the CH_3OH is evaporated. The resulting solution is 12% NaBH_4 in aq NaOH , which is itself an important commercial product; NaBH_4 is extracted from this solution, dried and recrystallized to a 97+% pure product².

One process employs a high-T, dry reaction of borax, sodium metal, H_2 and sand or borosilicate, Na and H_2O :



The NaBH_4 is extracted from the mass with aq NH_3 ; the resulting solution is fed into a drier that drives off the NH_3 and the NaBH_4 crystals are further dried and packaged².

The major process for the commercial production³ of LiAlH_4 utilizes the procedure in its original discovery^{4,5}:



where AlCl_3 as an ether slurry is fed into a reactor to which is added a LiH slurry⁶. An induction period ensues because an oxide forms, coating the LiH . This is overcome by adding seeds of LiAlH_4 before the AlCl_3 is added. Pure product is obtained from this process.

Other commercial processes include the preparation of NaAlH_4 from NaH and AlCl_3 followed by metathesis with LiCl , and a process utilizing reaction of the elements Li , Al and H_2 at 14.5 MPa and 100°C in the presence of a catalyst⁶. An extension of this method employs the use of 1:1 Al-Li alloys. In this process the alloy is shaken in tetrahydrofuran (THF) in an autoclave at 120–130°C and 10.1 MPa H_2 for 3 days⁷. Pure LiAlH_4 is obtained in 80% yield.

(L. BARTON)

5. A. J. Downs, P. D. P. Thomas, *J. Chem. Soc., Chem. Commun.*, 825 (1976).
6. A. J. Downs, P. D. P. Thomas, *J. Chem. Soc., Dalton Trans.*, 809 (1978).
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1.7.6. by Industrial Processes.

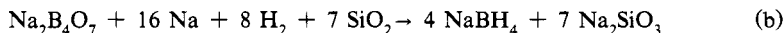
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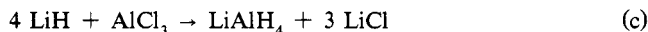
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2. R. C. Wade, in *Speciality Inorganic Chemicals*, Special Publication No. 40, The Royal Society of Chemistry, London, 1981, p. 25.
3. E. C. Ashby, *Adv. Inorg. Chem. Radiochem.*, 8, 283 (1966).
4. A. E. Finholt, A. C. Bond, H. I. Schlesinger, *J. Am. Chem. Soc.*, 69, 1199 (1947).
5. H. I. Schlesinger, A. E. Finholt, U.S. Pat. 2,576,311 (1951); *Chem. Abstr.*, 46, 2761 (1952).
6. M. Grayson, D. Eckroth, eds., *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Wiley-Interscience, New York, Vol. 11, 1980, p. 217.
7. H. Hoffman-La Roche, Br. Pat. 888,045 (1962); *Chem. Abstr.*, 56, 13,801 (1962).

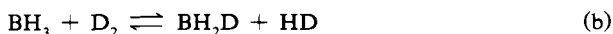
1.7.7. The Synthesis of Deuterium Derivatives

The reagents NaBD_4 and LiAlD_4 are available commercially, so compounds containing the deuterium-group III element bonds may be prepared by standard methods using these reagents. The NaBD_4 is prepared from NaD and $\text{B}(\text{OCH}_3)_3$, LiAlD_4 is prepared from LiD and AlCl_3 and LiGaD_4 is prepared from LiD and GaCl_3 .

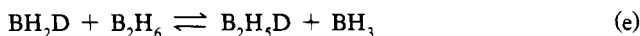
(L.BARTON)

1.7.7.1. by Isotopic Exchange.

The $[\text{BH}_4]^-$ ion undergoes exchange with D_2 at 5.07 MPa and 500°C to afford randomly deuterium-substituted products¹:



Also, B_2H_6 may be deuterated by treatment with $\text{D}_{2(\text{g})}$. Successive treatments for 24 h at 75°C afford² 98% B_2D_6 . Kinetics³ between 25 and 75°C reflect a $\frac{3}{2}$ order with respect to B_2H_6 and zero order with respect to D_2 . The reaction proceeds between BH_3 and D_2 on the walls of the reaction vessel with an activation energy of 91.3 kJ mol^{-1} . The mechanism is:



Exchange also occurs⁴ with T_2 , DT and TH . Self-exchange between B_2H_6 and B_2D_6 occurs, wherein rapid equilibrium between B_2H_6 and 2BH_3 is followed by a rate-determining collision between B_2D_6 and a BH_3 molecule^{6,7}.

Exchange between B_4H_{10} and B_2D_6 at 45°C may proceed by rapid selective deuteration at the 1,3-terminal positions⁸, followed by a slower process involving all other positions; however, D is found in the 2,4- and bridge positions⁹. Self-exchange in $\mu\text{-DB}_4\text{H}_9$ proceeds rapidly at the 1,3- and 2,4-(either axial or equatorial, but not both)-positions and more slowly at the remaining 2,4- and bridge-positions. The numbering system in B_4H_{10} is shown in Fig. 1.

Perdeuterated B_5H_9 may be prepared⁵ by reaction between B_5H_9 and D_2 in the presence of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ dehydrogenation catalysts at 25°C . By passage of B_5H_9 through the catalyst chamber in the presence of a 5:1 xs of D_2 , B_5D_9 in which 98.5% of the original H has been replaced by D is obtained after five passes.

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2. R. C. Wade, in *Speciality Inorganic Chemicals*, Special Publication No. 40, The Royal Society of Chemistry, London, 1981, p. 25.
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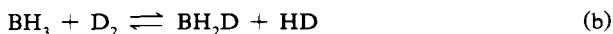
1.7.7. The Synthesis of Deuterium Derivatives

The reagents NaBD₄ and LiAlD₄ are available commercially, so compounds containing the deuterium-group III element bonds may be prepared by standard methods using these reagents. The NaBD₄ is prepared from NaD and B(OCH₃)₃, LiAlD₄ is prepared from LiD and AlCl₃ and LiGaD₄ is prepared from LiD and GaCl₃.

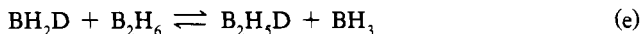
(L.BARTON)

1.7.7.1. by Isotopic Exchange.

The [BH₄]⁻ ion undergoes exchange with D₂ at 5.07 MPa and 500°C to afford randomly deuterium-substituted products¹:



Also, B₂H₆ may be deuterated by treatment with D_{2(g)}. Successive treatments for 24 h at 75°C afford² 98% B₂D₆. Kinetics³ between 25 and 75°C reflect a $\frac{3}{2}$ order with respect to B₂H₆ and zero order with respect to D₂. The reaction proceeds between BH₃ and D₂ on the walls of the reaction vessel with an activation energy of 91.3 kJ mol⁻¹. The mechanism is:



Exchange also occurs⁴ with T₂, DT and TH. Self-exchange between B₂H₆ and B₂D₆ occurs, wherein rapid equilibrium between B₂H₆ and 2 BH₃ is followed by a rate-determining collision between B₂D₆ and a BH₃ molecule^{6,7}.

Exchange between B₄H₁₀ and B₂D₆ at 45°C may proceed by rapid selective deuteration at the 1,3-terminal positions⁸, followed by a slower process involving all other positions; however, D is found in the 2,4- and bridge positions⁹. Self-exchange in μ -DB₄H₉ proceeds rapidly at the 1,3- and 2,4-(either axial or equatorial, but not both)-positions and more slowly at the remaining 2,4- and bridge-positions. The numbering system in B₄H₁₀ is shown in Fig. 1.

Perdeuterated B₅H₉ may be prepared⁵ by reaction between B₅H₉ and D₂ in the presence of Cr₂O₃-Al₂O₃ dehydrogenation catalysts at 25°C. By passage of B₅H₉ through the catalyst chamber in the presence of a 5:1 xs of D₂, B₅D₉ in which 98.5% of the original H has been replaced by D is obtained after five passes.

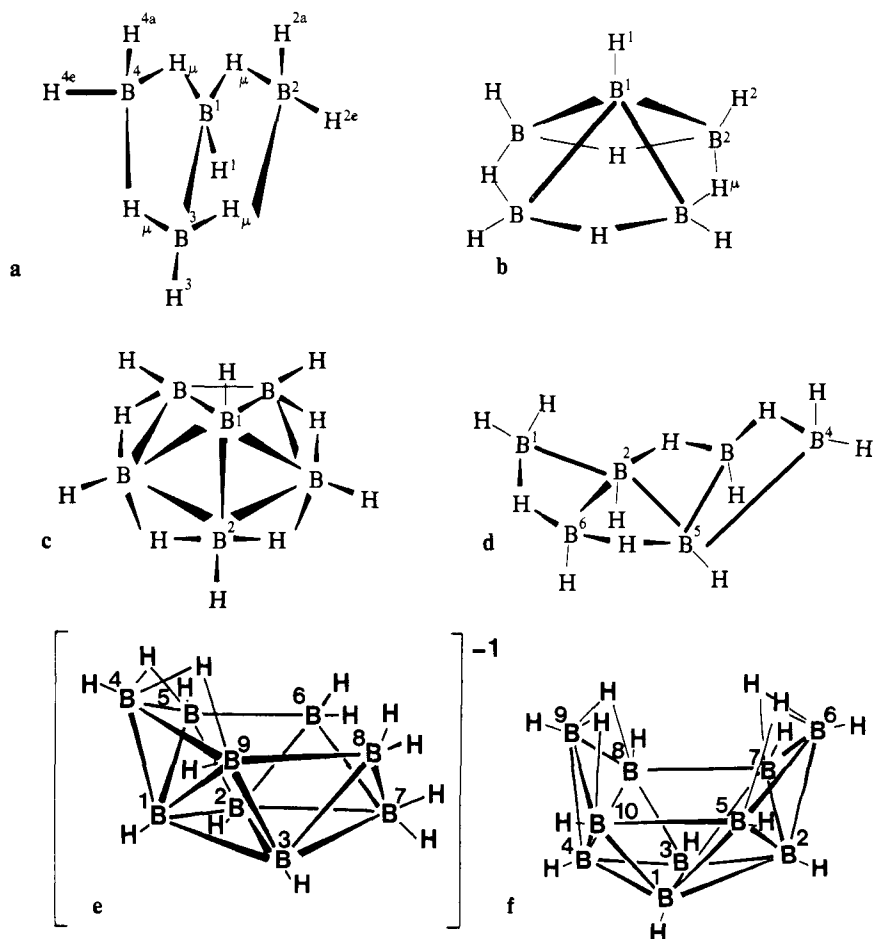


Figure 1. Atomic numbering scheme for borane species: a, B_4H_{10} ; b, B_5H_9 ; c, B_6H_{10} ; d, B_6H_{12} ; e, $[B_9H_{14}]^-$; f, $B_{10}H_{14}$. Where not indicated, terminal H atoms bear the same numbers as the B atoms to which they are bonded.

Pentaborane(9) and SiD_4 undergo hydrogen transfer at $125^\circ C$. The apical position in B_5H_9 is preferentially deuterated, but some traces of D also exchange with basal terminal hydrogens¹⁰. With B_2D_6 at $80^\circ C$, B_5H_9 undergoes rapid exchange of H for D in a process in which only terminal hydrogens are replaced^{11,12}. The rate for basal-terminal H-D exchange is the same as for apical-hydrogen exchange¹³. At $45^\circ C$ exchange of D for H between the bridging and basal terminal positions occurs in $(C_2H_5)_2O$ solns; however, similar exchange between the apical and basal terminal positions does not occur¹⁴, even at $95^\circ C$ after 15 h. This thermal rearrangement is a high-barrier process and 145 – $200^\circ C$ is required for the gas-phase reaction. Both the intra- and intermolecular processes require¹⁵ similarly high T.

Hexaborane(10) may be deuterated selectively in the basal terminal positions by treatment with B_2D_6 in ether at $-20^\circ C$. This is in contrast to the higher T required^{16,17} for B_5H_9 . Some H-D exchange occurs in the bridging position in B_6H_{10} , but either

higher T or catalysts may be involved¹⁸. Hexaborane(12) may be deuterated selectively by treatment with B_2D_6 at $-31^\circ C$ to afford 1,1,4,4-tetradeuteriohexaborane(12). Further reaction with liq B_2D_6 at $25^\circ C$ results¹⁹ in the complete deuteration of B_6H_{12} . Again, atom positions for B_6H_{10} and B_6H_{12} are given in Fig. 1.

Treatment of B_8H_{12} with liq B_2D_6 at $-30^\circ C$ forms $n-B_9H_{15}$ and $B_{10}H_{14}$, which reflect extensive nonspecific deuteration²⁰. This reaction proceeds initially by exchange of H for D in B_8H_{12} , and then the $B_8H_nD_{12-n}$ reacts more slowly with B_2D_6 to give $n-B_9H_nD_{15-n}$. The reaction of $n-B_9H_{15}$ with liq B_2D_6 at $27^\circ C$ yields a nonspecifically deuterated $B_{10}H_{14}$ and a deuterio- $n-B_9H_{15}$ with at least one terminal site not deuterated. This latter reaction does not occur at $-30^\circ C$; however, $B_{10}H_{14}$, formed from the reaction between $i-B_9H_{15}$ and B_2D_6 at $-30^\circ C$, is deuterated extensively.

Exchange between $B_{10}H_{14}$ and B_2D_6 occurs only in processes involving the terminal hydrogens²¹.

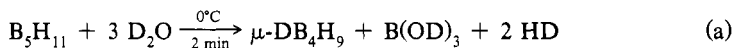
(L. BARTON)

1. E. E. Mesmer, W. L. Jolly, *J. Am. Chem. Soc.*, **84**, 2039 (1962).
2. A. B. Burg, *J. Am. Chem. Soc.*, **74**, 1340 (1952).
3. P. C. Maybury, W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).
4. J. S. Rigden, W. S. Koski, *J. Am. Chem. Soc.*, **83**, 3037 (1961).
5. H. J. Hrostowski, G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).
6. W. S. Koski, in *Borax to Boranes*, D. L. Martin, ed., Advances in Chemistry Series No. 32, American Chemical Society, Washington, DC, 1961, p. 78.
7. I. Shapiro, B. Keilen, *J. Am. Chem. Soc.*, **77**, 2663 (1955).
8. J. E. Todd, W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).
9. R. Schaeffer, L. G. Sneddon, *Inorg. Chem.*, **12**, 3098 (1972).
10. M. L. Thompson, R. Schaeffer, *Inorg. Chem.*, **7**, 1677 (1968).
11. W. S. Koski, J. J. Kaufman, L. Friedman, A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).
12. J. J. Kaufman, W. S. Koski, *J. Chem. Phys.*, **24**, 403 (1956).
13. W. S. Koski, J. J. Kaufman, P. C. Lauterbur, *J. Am. Chem. Soc.*, **79**, 2382 (1957).
14. J. A. Heppert, D. F. Gaines, *Inorg. Chem.*, **22**, 3155 (1983).
15. T. P. Onak, F. J. Gerhart, R. E. Williams, *J. Am. Chem. Soc.*, **85**, 1754 (1963).
16. J. C. Carter, N. L. H. Mock, *J. Am. Chem. Soc.*, **91**, 5891 (1969).
17. J. D. Odom, R. Schaeffer, *Inorg. Chem.*, **9**, 2157 (1970).
18. R. E. Williams, S. G. Gibbins, I. Shapiro, *J. Chem. Phys.*, **30**, 353 (1959).
19. A. L. Collins, R. Schaeffer, *Inorg. Chem.*, **9**, 2153 (1970).
20. R. Maruca, J. D. Odom, R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).
21. J. J. Kaufman, W. S. Koski, *J. Am. Chem. Soc.*, **78**, 5774 (1956).

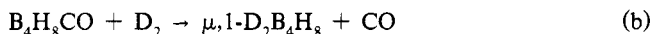
1.7.7.2. by Isotopic Enrichment Using Chemical Reactions.

Fully deuterated B_2H_6 may be obtained by treatment¹ of commercially available $NaBD_4$ with hot H_3PO_4 and also by treatment^{2,4} of $LiAlD_4$ with $F_3B \cdot O(C_2H_5)_2$.

Tetraborane(10) deuterated in a bridge position is prepared⁵ by treatment of $K[B_4H_9]$ with DCl at $-78^\circ C$. When the reaction mixture is warmed over a period of several hours, deuteration at terminal positions is also evident^{5,6}. The species $\mu\text{-}DB_4H_9$ is also prepared⁷ by cleavage of B_5H_{11} with D_2O in a sealed tube at $0^\circ C$:



Treatment of B_4H_8CO with D_2 at 0.2 kPa affords 1, μ -dideuteriotetraborane(10) in yields⁸ of $\leq 20\%$:



148 1.7. Formation of Bonds between Hydrogen and B, Al, Ga, In, Tl
 1.7.7. The Synthesis of Deuterium Derivatives

higher T or catalysts may be involved¹⁸. Hexaborane(12) may be deuterated selectively by treatment with B₂D₆ at -31°C to afford 1,1,4,4-tetradeuteriohexaborane(12). Further reaction with liq B₂D₆ at 25°C results¹⁹ in the complete deuteration of B₆H₁₂. Again, atom positions for B₆H₁₀ and B₆H₁₂ are given in Fig. 1.

Treatment of B₈H₁₂ with liq B₂D₆ at -30°C forms n-B₉H₁₅ and B₁₀H₁₄, which reflect extensive nonspecific deuteration²⁰. This reaction proceeds initially by exchange of H for D in B₈H₁₂, and then the B₈H_nD_{12-n} reacts more slowly with B₂D₆ to give n-B₉H_nD_{15-n}. The reaction of n-B₉H₁₅ with liq B₂D₆ at 27°C yields a nonspecifically deuterated B₁₀H₁₄ and a deuterio-n-B₉H₁₅ with at least one terminal site not deuterated. This latter reaction does not occur at -30°C; however, B₁₀H₁₄, formed from the reaction between i-B₉H₁₅ and B₂D₆ at -30°C, is deuterated extensively.

Exchange between B₁₀H₁₄ and B₂D₆ occurs only in processes involving the terminal hydrogens²¹.

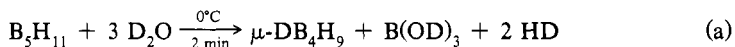
(L. BARTON)

1. E. E. Mesmer, W. L. Jolly, *J. Am. Chem. Soc.*, **84**, 2039 (1962).
2. A. B. Burg, *J. Am. Chem. Soc.*, **74**, 1340 (1952).
3. P. C. Maybury, W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).
4. J. S. Rigden, W. S. Koski, *J. Am. Chem. Soc.*, **83**, 3037 (1961).
5. H. J. Hrostowski, G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).
6. W. S. Koski, in *Borax to Boranes*, D. L. Martin, ed., Advances in Chemistry Series No. 32, American Chemical Society, Washington, DC, 1961, p. 78.
7. I. Shapiro, B. Keilen, *J. Am. Chem. Soc.*, **77**, 2663 (1955).
8. J. E. Todd, W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).
9. R. Schaeffer, L. G. Sneddon, *Inorg. Chem.*, **12**, 3098 (1972).
10. M. L. Thompson, R. Schaeffer, *Inorg. Chem.*, **7**, 1677 (1968).
11. W. S. Koski, J. J. Kaufman, L. Friedman, A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).
12. J. J. Kaufman, W. S. Koski, *J. Chem. Phys.*, **24**, 403 (1956).
13. W. S. Koski, J. J. Kaufman, P. C. Lauterbur, *J. Am. Chem. Soc.*, **79**, 2382 (1957).
14. J. A. Heppert, D. F. Gaines, *Inorg. Chem.*, **22**, 3155 (1983).
15. T. P. Onak, F. J. Gerhart, R. E. Williams, *J. Am. Chem. Soc.*, **85**, 1754 (1963).
16. J. C. Carter, N. L. H. Mock, *J. Am. Chem. Soc.*, **91**, 5891 (1969).
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18. R. E. Williams, S. G. Gibbins, I. Shapiro, *J. Chem. Phys.*, **30**, 353 (1959).
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20. R. Maruca, J. D. Odom, R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).
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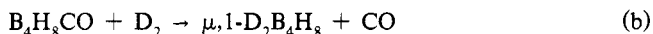
1.7.7.2. by Isotopic Enrichment Using Chemical Reactions.

Fully deuterated B₂H₆ may be obtained by treatment¹ of commercially available NaBD₄ with hot H₃PO₄ and also by treatment^{2,4} of LiAlD₄ with F₃B·O(C₂H₅)₂.

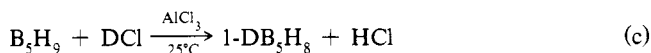
Tetraborane(10) deuterated in a bridge position is prepared⁵ by treatment of K[B₄H₉] with DCl at -78°C. When the reaction mixture is warmed over a period of several hours, deuteration at terminal positions is also evident^{5,6}. The species μ-DB₄H₉ is also prepared⁷ by cleavage of B₅H₁₁ with D₂O in a sealed tube at 0°C:



Treatment of B₄H₈CO with D₂ at 0.2 kPa affords 1,μ-dideuteriotetraborane(10) in yields⁸ of ≤20%:



Pentaborane(9) may be deuterated selectively at the apical position by treatment with DCl in the presence of AlCl₃ at RT. 1-Deuteration is complete after 2 h, and 1-DB₅H₈ containing 90% D at the 1-position may be prepared⁹:



This reaction does not occur in the absence of AlCl₃, nor may 1-CH₃B₅H₈ be deuterated by this process⁹. The 1-DB₅H₈ also may be prepared¹⁰ by treatment of B₅H₉ with C₆D₆ in the presence of a catalytic amount of AlCl₃ at 25°C for 24 h. The method is quantitative, and pure 1-DB₅H₈ is isolated by trap-to-trap distillation at -78° and -196°C, the desired product collecting in the colder trap. Pentaborane(9) may be deuterated selectively¹¹ in a bridging position by treatment of Li[B₅H₈] with DCl at -78°C. Intramolecular H-D exchange¹² takes place in 1-DB₅H₈ catalyzed by 2,6-dimethylpyridine at 25°C. The intermediate in the process is an electron-pair base adduct, and exchange occurs with all H positions in the B₅H₈ moiety.

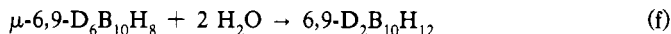
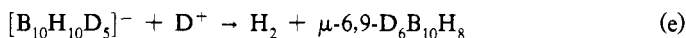
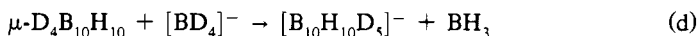
The 2-DB₅H₈ derivative is prepared by treatment of 2-ClB₅H₈ with (n-C₄H₉)₃SnD in a sealed tube under N₂. The reactor is allowed to warm from -78° to 25°C over several hours. The product is isolated by vacuum line distillation through -63°, -96° and -196°C U-traps. The 2-DB₅H₈ is isolated in the -96°C trap¹⁰.

Hexaborane(10) may be prepared with nonspecific deuteration by shaking B₆H₁₂ with a fourfold xs of D₂O in (C₂H₅)₂O for 1 h. The average composition of the product¹³ is B₆H_{7.3}D_{2.7}.

The B ion in K[B₉H₁₄] undergoes acid-catalyzed exchange of hydrogens at the 4-, 6- and 8-positions¹⁴, e.g., when K[B₉H₁₄] in D₂O is made 10⁻³ M in DCl, deuteration at the 4-, 6- and 8-positions occurs within 20 min (see Fig. 1, §1.7.7.1, for numbering scheme). Proton NMR studies indicate that bridge hydrogens do not exchange under these conditions; however, after a period of several hours at 25°C some collapse of the bridge-region resonances is observed, indicating slow μ-H-D exchange by a secondary process. In solutions 10⁻³ M in NaOD, complete, rapid exchange of bridge hydrogens occurs. When 1 M NaOD is used, both the bridge and the 4-, 6- and 8-terminal positions deuterate. Exchange between bridge and terminal positions in this anion involves only the 4-, 6- and 8-terminal positions; D originally in bridge positions exchanges¹⁴ with terminal H at positions 4, 6 and 8 over a period of 3-4 h.

Decaborane(14) may be prepared with selective deuteration in several different positions. Treatment of B₁₀H₁₄ in dioxane with D₂O at 25°C results in initial substitution in the bridge position¹⁵⁻¹⁷. After ca. 10 min, flash evaporation of the solution affords μ-D₄B₁₀H₁₀ containing an average of 3.5 D per molecule. After extended periods, exchange occurs between the bridge and the terminal hydrogen positions; in no case are more than eight D atoms incorporated. Both the 5,7,8,10- and the 6,9-terminal positions participate in this base-catalyzed exchange. The relative rates¹⁸ of base-catalyzed H-D exchange in B₁₀H₁₄ are 6,9 > 5,7,8,10 > 1,3 and 2,4. Treatment in ether of the salt Na[B₁₀H₁₃], prepared from NaH and B₁₀H₁₄, with DCl affords μ-DB₁₀H₁₃ quantitatively¹⁶; DCl also reacts with B₁₀H₁₄ in basic solvents at 25°C to effect substitution of D for H at the bridge and 5,6,7,8,9,10-terminal positions. Thus, dioxane 5.0 M in DCl and 5 × 10⁻² M in B₁₀H₁₄, left to equilibrate at 25°C for 404 h, affords B₁₀D₁₀H₄ in which the bridge and 5,6,7,8,9,10-terminal positions are deuterated completely^{20,22}. Shorter reaction times allow the μ-D₄B₁₀H₁₀ species to be isolated^{19,20}. The species μ-1,2,3,4-D₈B₁₀H₆ is prepared²¹ by shaking μ-D₄B₁₀H₁₀ in a D₂O-CH₃CN (1:1 by vol) solution for 20 min. It is possible to prepare B₁₀H₁₄ with deuterium at only the 6-

and 9-positions. The reaction between $\mu\text{-D}_4\text{B}_{10}\text{H}_{10}$ and NaBD_4 in glyme under N_2 affords $[\text{B}_{10}\text{H}_{10}\text{D}_5]^-$. Treatment with DCl affords $\text{B}_{10}\text{H}_8\text{D}_6$ and H_2 , and reaction with H_2O -dioxane affords²³ $6,9\text{-D}_2\text{B}_{10}\text{H}_{12}$:



Electrophilic deuterium exchange may be effected²⁰ in $\text{B}_{10}\text{H}_{14}$ by xs DCl in CS_2 in the presence of AlCl_3 to give $1,2,3,4\text{-D}_4\text{B}_{10}\text{H}_{10}$ after 36 h. Repetition four times allows $2,4,5,7,8,10\text{-D}_6\text{B}_{10}\text{H}_8$ to be isolated¹⁹. A similar reaction allowed to proceed for several days affords²¹ $1,2,3,4,5,7,8,10\text{-D}_8\text{B}_{10}\text{H}_6$. When HCl is bubbled through $1,2,3,4,5,7,8,10\text{-D}_8\text{B}_{10}\text{H}_6$ in CS_2 , in the presence of AlCl_3 for 36 h, the species $5,7,8,10\text{-D}_4\text{B}_{10}\text{H}_{10}$ may be isolated. If $\mu\text{-D}_4\text{B}_{10}\text{H}_{10}$ is allowed to react with an xs of DCl in CS_2 in the presence of AlCl_3 at 25°C for 6 days, $\mu,1,2,3,4,5,7,8,10\text{-D}_{12}\text{B}_{10}\text{H}_2$ may be isolated²¹. The labeling scheme for $\text{B}_{10}\text{H}_{14}$ is found in Fig. 1, §1.7.7.1.

(L. BARTON)

1. R. Maruca, J. D. Odom, R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).
2. J. E. Todd, W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2139 (1959).
3. A. D. Norman, R. Schaeffer, A. B. Bayliss, G. A. Pressley Jr., F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 2151 (1966).
4. R. Schaeffer, L. G. Sneddon, *Inorg. Chem.*, **11**, 3098 (1972).
5. A. C. Bond, M. L. Pinsky, *J. Am. Chem. Soc.*, **92**, 7585 (1970).
6. A. C. Bond, M. L. Pinsky, *Inorg. Chem.*, **12**, 605 (1963).
7. A. D. Norman, R. Schaeffer, *Inorg. Chem.*, **4**, 1225 (1965).
8. A. D. Norman, R. Schaeffer, *J. Am. Chem. Soc.*, **88**, 1143 (1966).
9. T. P. Onak, R. E. Williams, *Inorg. Chem.*, **1**, 106 (1962).
10. J. A. Heppert, D. F. Gaines, *Inorg. Chem.*, **22**, 3155 (1983).
11. D. F. Gaines, T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 3375 (1967).
12. T. P. Onak, F. J. Gerhart, R. E. Williams, *J. Am. Chem. Soc.*, **85**, 1754 (1963).
13. J. D. Odom, R. Schaeffer, *Inorg. Chem.*, **9**, 2157 (1970).
14. P. C. Keller, *Inorg. Chem.*, **9**, 75 (1970).
15. M. F. Hawthorne, J. J. Miller, *J. Am. Chem. Soc.*, **80**, 754 (1958).
16. J. J. Miller, M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 4501 (1959).
17. M. Hillman, *J. Am. Chem. Soc.*, **82**, 1096 (1960).
18. I. Shapiro, M. Lustig, R. E. Williams, *J. Am. Chem. Soc.*, **81**, 838 (1959).
19. J. A. Dupont, M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 838 (1959).
20. J. A. Dupont, M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 1804 (1962).
21. F. Hanousek, B. Stibi, S. Hermanek, J. Plešek, *Coll. Czech. Chem. Commun.*, **38**, 1312 (1973).
22. E. Hoel, M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 6388 (1973).
23. J. A. Slater, A. D. Norman, *Inorg. Chem.*, **10**, 205 (1971).

1.8. Formation of Bonds between Hydrogen and Metals of Group IA (Li, Na, K, Rb, Cs, Fr) or IIA (Be, Mg, Ca, Sr, Ba, Ra)

1.8.1. Introduction

Compounds in which hydrogen is bonded to the alkali and alkaline-earth metals except beryllium are prepared by direct synthesis from the metals or amalgams. Beryllium hydride is prepared by pyrolysis or reduction of organic derivatives.

(J. J. ZUCKERMAN, ED.)

1.8.2. Alkali-Metal Hydrides

The alkali-metal hydrides are colorless solids that crystallize in the NaCl cubic system. They are saline or ionic hydrides containing an M^+ cation ($M = \text{Li, Na, K, Rb, Cs}$) and the H^- hydride anion, the dimensions of which are comparable to those of the fluoride ion¹.

Preparation is by direct synthesis. The H_2 must be free of O_2 and of H_2O , which react rapidly and irreversibly with the alkali metals and their hydrides. Although less reactive, the volatile hydrides present in H_2 (H_2S , NH_3 , CH_4 , C_2H_2) also should be eliminated. Finally, in the synthesis of LiH , the presence of N_2 must be avoided.

The conditions for preparing LiH are different from those of the other alkali hydrides because of its high stability, making it similar to the alkaline-earth hydrides. This hydride, therefore, is discussed separately.

(A. HEROLD, J.F. MARECHE)

1.8.2.1. Lithium Hydride

Lithium hydride is an industrial product utilized in organic synthesis, preparation of other hydrides, etc. The hydride, deuteride and tritide of Li play a role in the nuclear industry.

(i) Direct Synthesis. This method differs little from that first utilized² in 1896. The Li, contained in Fe, is heated under H_2 . The reaction starts at RT but becomes rapid only above the mp of the metal. As shown by the fusion diagram of the Li–LiH system³ (Fig. 1), the hydride is partially soluble in the liq metal, which helps the reaction. It is also favored by the density of LiH ($0.7\text{--}0.8 \text{ g/cm}^{-3}$) which is greater than that of Li ($\sim 0.5 \text{ g/cm}^{-3}$), so that LiH falls to the bottom of the reactor and frees the surface of the metal. Nevertheless, to obtain complete hydrogenation, T must be higher than the mp of the hydride (689°C), but lower than the T of the monotectic plateau of the Li–LiH system.

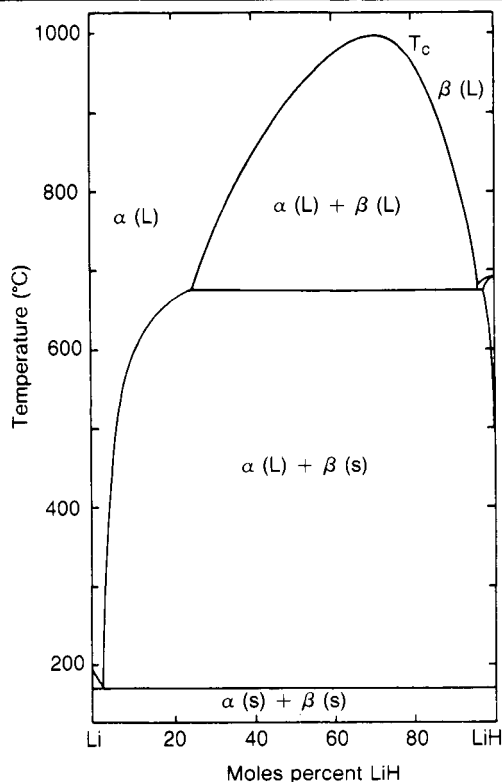


Figure 1. Diagram of the Li-LiH system.

At this T, the H_2 pressure for the pure hydride is only 23.7 torr (3.16×10^3 Pa) and, based on the equations of ref. 4, atm P is attained only at 889°C.

The hydride therefore, can be melted easily under H_2 without decomposing.

Industrially, the operation is carried out on 20–30 kg of metal at a time³. The metal is melted under vacuum; then the H_2 is progressively introduced. The heat given off by:



is ca. 80 kJ/mol⁻¹, sufficient to maintain the T without external heating. The efficiency of converting the metal into the hydride is $\geq 98\%$.

Single crystals are prepared starting from the melted hydride⁵⁻⁷, or also by growth in organic solvents, using three methods:

1. Vertical drawing from a bath of melted hydride using a metallic rod⁵.
2. Vertical downward movement of a cylindroconical crucible containing the molten hydride from a hot zone to a cold one; the crystallization begins at the point of the cone and progresses throughout the whole crucible^{6,7}.
3. Growth in solvents, the best being CCl_4 , which dissolves 2×10^{-4} g L⁻¹ of hydride⁸.

(ii) Other Syntheses. Complete hydrogenation of the metal can be obtained below 350°C in the presence of catalysts⁹ such as WS₂ or MoS₂, but these introduce impurities into the product.

Lowering the T to below the mp of the metal by the use of an electric discharge¹⁰ under low P is not a practical means of preparation.

More practical is the synthesis of the hydride under an H₂ current by heating an amalgam obtained by the electrolysis of a solution of chlorides with an Hg cathode¹¹. The Li combines with the H₂, whereas the Hg is carried out and condensed. This method, which avoids preparation of the metal by high-T electrolysis, is only at the testing stage.

(iii) Lithium Deuteride and Tritide. Although the dissociation P of Li deuteride and tritide are different from those of the protide, the preparation conditions are the same^{12,13}.

The tritide is special because the isotope has a half-life of 12.26 y, and LiT can be obtained by isotopic exchange:



or by neutron bombardment¹⁴⁻¹⁶ of LiH.

(A. HEROLD, J.F. MARECHE)

1. C. B. Magee, in *Metal Hydrides*, W. M. Mueller, ed., Academic Press, New York, 1968, p. 165.
2. A. Guntz, *C. R. Hebd. Seances Acad. Sci.* 122, 244; 123, 1273 (1896).
3. C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor, R. Seales, *J. Phys. Chem.*, 62, 220 (1958).
4. C. E. Messer, *USAEC Report NYO-9470*, Tufts Univ., (1960). A report on LiH.
5. J. Tuffier, S. Bedere, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 280, 337 (1975).
6. V. D. Pirogev, S. O. Cholakh, F. F. Gavilov, G. I. Philipenko, B. V. Schudgin, S. I. Somov, N. I. Kanunnikov, B. V. Vlasov, V. G. Ovechkin, *Fiz. Khim. Gidridov*, 155, 72 (1972); *Chem. Abstr.*, 83, 185,69 (1975).
7. C. E. Holcombe, D. H. Johnson, *J. Cryst. Growth*, 19, 53 (1973).
8. R. Suchansko, K. Kulichi, W. Cetner, *Biul. Wojsk. Akad. Tech.*, 23, 538 (1974); *Chem. Abstr.*, 82, 205,257 (1975).
9. S. Landa, F. Petri, J. Vit, V. Prochazka, J. Mostecky, *Sb. Vys. Sk. Chem.-Technol. Praze, Oddil Fak. Anorg. Org. Technol.*, 495 (1958); *Chem. Abstr.*, 55, 6225 (1961).
10. United Aircraft Corp., Br. Pat. 1,004,769 (1960); *Chem. Abstr.*, 63, 15,893 (1965).
11. J. Novotny, M. Skolova, Czech. Pat. 86,588 (1957); *Chem. Abstr.*, 54, 9229 (1960).
12. F. K. Neumann, O. N. Salmon, USAEC Report KA PL 1667, Knolls Atomic Power Laboratory, 1956; *Chem. Abstr.*, 51, 9280 (1957).
13. E. Welekis, *J. Nucl. Mater.*, 79, 20 (1979); *Chem. Abstr.*, 90, 93,904 (1979).
14. V. A. Maroni, E. Velekis, E. H. Van Deventer, *Proc. Sympos. Tritium Technol., Relat. Fusion Reactor Syst.*, p. 120 (1974); *Chem. Abstr.*, 85, 130,698 (1976).
15. L. A. Zaputryacva, O. N. Pavlov, A. T. Uverskaya, M. S. Fadecva, *Trudy Gos. Inst. Prikl. Khim.*, 45, 97 (1960); *Chem. Abstr.*, 56, 2141 (1962).
16. M. Ziclinsky, *Nukleonika* 7, 789 (1962); *Chem. Abstr.*, 59, 5015 (1963).

1.8.2.2. Sodium, Potassium, Rubidium and Cesium Hydrides

These four compounds form a homogeneous group, and their means of preparation are similar.

Sodium hydride is used industrially in organic synthesis; the annual production is several million tons. Utilized much less, KH is also commercial, whereas RbH and CsH are laboratory products.

1.8. Formation of Bonds between Hydrogen and Group IA or IIA Metals 153

1.8.2. Alkali-Metal Hydrides

(ii) Other Syntheses. Complete hydrogenation of the metal can be obtained below 350°C in the presence of catalysts⁹ such as WS₂ or MoS₂, but these introduce impurities into the product.

Lowering the T to below the mp of the metal by the use of an electric discharge¹⁰ under low P is not a practical means of preparation.

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3. C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor, R. Seales, *J. Phys. Chem.*, 62, 220 (1958).
4. C. E. Messer, *USAEC Report* NYO-9470, Tufts Univ., (1960). A report on LiH.
5. J. Tuffier, S. Bedere, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 280, 337 (1975).
6. V. D. Pirogev, S. O. Cholak, F. F. Gavilov, G. I. Philipenko, B. V. Schudgin, S. I. Somov, N. I. Kanunnikov, B. V. Vlasov, V. G. Ovechkin, *Fiz. Khim. Gidridov*, 155, 72 (1972); *Chem. Abstr.*, 83, 185,69 (1975).
7. C. E. Holcombe, D. H. Johnson, *J. Cryst. Growth*, 19, 53 (1973).
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9. S. Landa, F. Petri, J. Vit, V. Prochazka, J. Mostecky, *Sb. Vys. Sk. Chem.-Technol. Praz, Oddil Fak. Anorg. Org. Technol.*, 495 (1958); *Chem. Abstr.*, 55, 6225 (1961).
10. United Aircraft Corp., Br. Pat. 1,004,769 (1960); *Chem. Abstr.*, 63, 15,893 (1965).
11. J. Novotny, M. Skolova, Czech. Pat. 86,588 (1957); *Chem. Abstr.*, 54, 9229 (1960).
12. F. K. Neumann, O. N. Salmon, USAEC Report KA PL 1667, Knolls Atomic Power Laboratory, 1956; *Chem. Abstr.*, 51, 9280 (1957).
13. E. Welekis, *J. Nucl. Mater.*, 79, 20 (1979); *Chem. Abstr.*, 90, 93,904 (1979).
14. V. A. Maroni, E. Velekis, E. H. Van Deventer, *Proc. Sympos. Tritium Technol., Relat. Fusion Reactor Sys.*, p. 120 (1974); *Chem. Abstr.*, 85, 130,698 (1976).
15. L. A. Zaputryayeva, O. N. Pavlov, A. T. Uverskaya, M. S. Fadecva, *Trudy Gos. Inst. Prikl. Khim.*, 45, 97 (1960); *Chem. Abstr.*, 56, 2141 (1962).
16. M. Ziclinsky, *Nukleonika* 7, 789 (1962); *Chem. Abstr.*, 59, 5015 (1963).

1.8.2.2. Sodium, Potassium, Rubidium and Cesium Hydrides

These four compounds form a homogeneous group, and their means of preparation are similar.

Sodium hydride is used industrially in organic synthesis; the annual production is several million tons. Utilized much less, KH is also commercial, whereas RbH and CsH are laboratory products.

154 1.8. Formation of Bonds between Hydrogen and Group IA or IIA Metals
 1.8.2. Alkali-Metal Hydrides
 1.8.2.2. Sodium, Potassium, Rubidium and Cesium Hydrides

TABLE 1. KINETICS OF THE REACTION OF H_2 WITH THE
 ALKALI METALS (v = SPEED OF THE REACTION AND 100°C AND 1 ATM).

Metal	Na	K	Rb	Cs
v at 100°C	0.00061	0.0105	0.062	0.53
$E_a(\text{kJ})^a$	71.5	49.4	39.6	27.7

^a Activation energy.

(i) $M + \frac{1}{2} H_2 \rightarrow MH$ ($M = \text{Na, K, Rb, Cs}$). The combination of Na and K with H_2 is reversible¹. The data in Table 1 give the orders of magnitude of the rates when dissociation of the hydrides is negligible². At 100°C , the speed rapidly increases $\text{Na} < \text{K} < \text{Rb} < \text{Cs}$, and the activation energy varies in the opposite order.

The four hydrides are dissociated easily by heat. Based on ref. 2, Table 2 gives the enthalpies of formation of 1 mol of solid hydride starting from H_2 gas and the liq metal deduced from the equilibrium P. It also gives the T , θ , in $^\circ\text{C}$, for which this P attains 1 atm. Less stable than LiH, these four hydrides dissociate without melting; they are only slightly soluble in the metals at $\theta^\circ\text{C}$.

The system Na-NaH under P at higher T shows a miscibility of the two phases³. At sufficiently high P and T the hydrides can be melted⁴: 107.3 atm and 638°C for NaH; 67.3 atm and 619°C for KH; 147.5 atm and 585°C for RbH and 31.5 atm and 528°C for CsH.

These data explain the difficulties encountered in completing the reaction between H_2 and the alkali metals other than Li. Under atm P, the hydride, which does not wet the metal or dissociate, slowly forms a superficial layer, the low permeability of which stops the reaction. The synthesis of pure hydrides however, is possible by vapor- and liquid-phase methods.

(ii) Direct Vapor-Phase Synthesis of the Hydrides. The homogeneous synthesis can be carried out by heating the alkali metal above the hydride dissociation T under a flow of H_2 ; the vapor is carried away by the gas and combines with the H_2 in a cooler zone of the reactor, giving hydride particles that remain in suspension in the gas. Electrostatic filtering⁵ can be used to separate them, but it is more efficient to clean the gas in a column using an organic liquid⁶.

Pure hydrides can be obtained in the laboratory by reacting the metal vapor with H_2 in contact with a wall and, therefore, in a heterogeneous phase². The apparatus in Fig. 1 is derived from that used to prepare pure hydrides⁷. The reactor is a horizontal borosilicate glass tube, a few cm in diameter; the lower portion is heated by a half-cylindrical oven. The $T = T_1$ of the metal contained in an Fe or Ni nacelle is lower than the dissociation T of the hydride, so that the hydride covers the metal. The system is not in equilibrium, however, because of the gradient between T_1 and T_2 of the upper wall of the tube ($T_1 > T_2$). The hydride layer constantly gives off vapor, which com-

TABLE 2. THERMODYNAMIC DATA² FOR THE REACTION $M_{(L)} + \frac{1}{2} H_{2(G)} \rightleftharpoons MH_{(S)}$

Metal	Na	K	Rb	Cs
$-\Delta H$ (kJ)	58.4	59.1	54.4	56.4
$\theta^\circ\text{C}$ (1 atm)	420	427	364	389

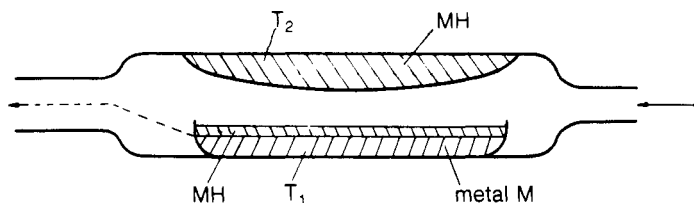


Figure 1. Direct synthesis of the alkali-metal hydrides by vapor-phase reaction in a T gradient.

binates with the H_2 on contact with the upper wall or with the hydride that covers it. At the same time that it dissociates in the upper portion, the hydride layer covering the metal is reformed from the latter, which can be transformed entirely into hydride deposited on the upper wall of the reactor. The nacelle can be withdrawn, e.g., with a magnet, and the tube sealed.

This process, also utilized for the synthesis of deuterides⁸, allows small quantities of pure hydrides to be obtained in the laboratory. The reaction speed, low for Na, a metal of low volatility, increases with the T_1 of the metal. This can be increased without dissociating the hydride layer at the metal surface here (the hydride formed on the upper wall of the tube is mixed with metal) by increasing the P to 2 or 3 atm.

(iii) Direct Liquid-Phase Synthesis of the Hydrides. As with Li, the other melted alkali metals can be hydrogenated⁹ above their mp, for NaH at 636–670°C and 68–100 atm; for CsH, 529–550°C, under 33–50 atm. The bulk hydride is obtained after cooling.

Below the mp of the hydride, the metal–gas contact surface, covered with an impermeable layer of hydride, must be renewed constantly for complete hydrogenation. This is done through agitation in the presence of a solid or liquid dispersant.

The best solid dispersant is the hydride itself. Liquid metal is introduced progressively into the agitated reactor containing the hydride from a previous preparation at 300°C under 20–30 atm H_2 . At the end of the operation, half the hydride in the reactor is withdrawn in order to restart the operation^{10–12}. The hydrogenation efficiency is 95–97%. This industrial technique furnishes hydride free of organic compounds.

The specific surface of the hydride can be increased¹³ by mixing CO with the H_2 and adding¹⁴ 0.1% MoS_2 and WS_2 lowers the reaction T .

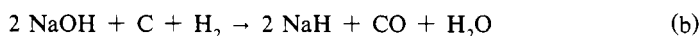
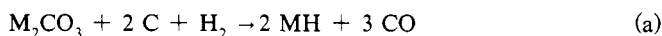
The simplest and most used industrial synthesis of NaH and KH consists in reacting 2–3 atm of H_2 (at ca. 300°C) with a dispersion of 50% Na or 25% K (by wt) in an inert liquid (mineral oil or kerosene), also at ca. 300°C^{11,15,16}. The conversion efficiency can reach 98%. The hydride can be conserved and manipulated in the form of a dispersion in the inert liquid. To obtain it dry, it is filtered and washed with a volatile solvent, such as petroleum ether. The synthesis can be accelerated by adding activating agents to the oil, such as anthracene or ortho-xylene, which act through the intermediate formation of π complexes with the alkali metal.

This method is employed for NaH in the laboratory at 200–220°C, using cyclic or noncyclic saturated hydrocarbons (C_7 – C_9) as dispersing agents.

Hydrogen acts¹⁷ under pressure on the amides $MNHR$ ($M = Na, K$) derived from primary amines C_1 – C_4 at ca. 90–100°C.

(iv) Sodium Hydride Synthesis Starting from an Amalgam. The industrial preparation of NaH starting from an amalgam^{18,19} is not used because of the low concentration of Na in the liquid amalgams.

(v) Synthesis Starting from Carbonates or Hydroxides. The reactions^{20,21}:



are not utilized.

(A. HEROLD, J.F. MARECHE)

1. J. L. Gay Lussac, L. J. Thenard, *Recherches Physicochim.*, 1, 176 (1811).
2. A. Herold, *Ann. Chim. (Paris)*, 6, 536 (1951).
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1.8.3. Alkaline-Earth Metal Hydrides

Calcium, Sr, Ba and presumably Ra react directly with H_2 to form ionic hydrides that have the orthorhombic PbCl_2 structure resembling the heavier alkaline-earth halides (e.g., BaCl_2 , BaBr_2 , BaI_2 , SrBr_2).

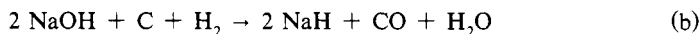
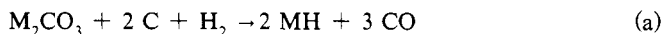
Beryllium hydride is covalent, similar to hydrides formed by the group IB–VB elements. Magnesium hydride is a borderline case; it can be formed by direct reaction of Mg metal and H_2 as well as by the procedures used to prepare covalent hydrides (see below).

(G.G. LIBOWITZ)

1.8.3.1. Beryllium Hydride

Beryllium hydride cannot be formed by direct reaction with H_2 . Techniques used to prepare solid, amorphous Be hydride never yield pure BeH_2 . Pyrolysis of di-t-

156 1.8. Formation of Bonds between Hydrogen and Group IA or IIA Metals

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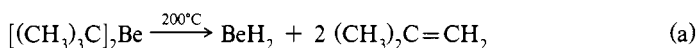
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(G.G. LIBOWITZ)

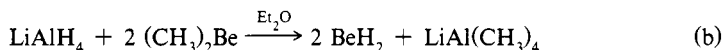
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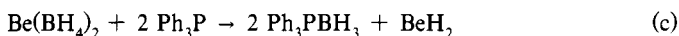
butylberyllium etherate yields a product containing 97 mol% BeH₂, the remainder being mostly ether¹:



If ether-free di-*t*-butylberyllium is pyrolyzed, the remaining impurity contains unreacted *t*-butyl groups². Beryllium hydride is also prepared by reacting LiAlH₄ with dimethylberyllium³:



and by removing BH₃ from Be(BH₃)₂ with triphenylphosphine⁴:



Residual impurities consisting of solvent, unreacted species or products of side reactions are present, although there are claims of pure BeH₂ from processes using Eq. (c)⁵.

Beryllium hydride prepared by these methods is an amorphous polymer, and IR spectra⁴ indicate long-chain bridge bonding.

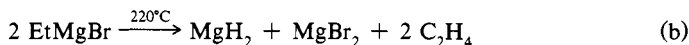
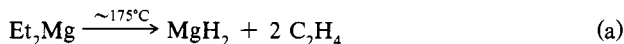
Crystalline BeH₂ is formed⁶ by high-P compaction-fusion of amorphous BeH₂ (prepared by pyrolysis of di-*t*-butylberyllium etherate). Pressures ≥ 275 MPa ($T \geq 200^\circ\text{C}$) and temperatures $> 130^\circ\text{C}$ ($P \geq 620$ MPa) are required. Crystallization is catalyzed by 0.5–2.5 mol% Li. A hexagonal phase is observed below 195°C , and a phase of unknown structure is predominant above that T .

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1.8.3.2. Magnesium Hydride

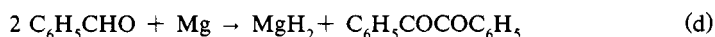
Magnesium hydride can be prepared by thermal decomposition of organometallic compounds¹ similar to reaction (a) (§1.8.3.1) for the preparation of BeH₂, e.g.:



or by metathesis with LiAlH₄ similar to reaction (b) (§1.8.3.1)²:



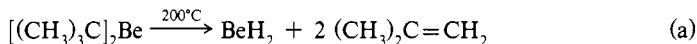
but it is impossible to remove the last traces of ether without decomposing the hydride. The hydride may be prepared³ by reacting acetaldehyde or benzaldehyde with Mg:



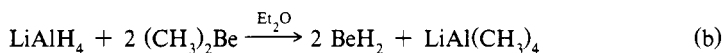
1.8. Formation of Bonds between Hydrogen and Group IA or IIA Metals 157

1.8.3. Alkaline-Earth Metal Hydrides

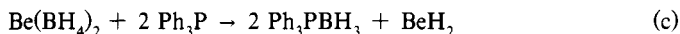
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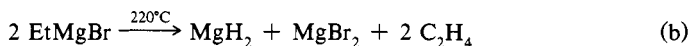
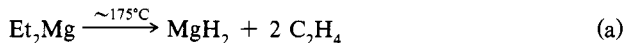
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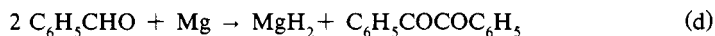
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but it is impossible to remove the last traces of ether without decomposing the hydride. The hydride may be prepared³ by reacting acetaldehyde or benzaldehyde with Mg:



Direct reaction of Mg and H_2 at elevated T and P yields MgH_2 . The rate is slow, and the process is difficult to carry to completion because the metal particles become coated with a dense layer of the hydride, through which the H_2 must diffuse. If the T is raised to increase the diffusion rate, the dissociation P is also increased and, for the reaction to proceed, the ambient H_2 P must exceed the dissociation P; e.g., 40 MPa and over 500°C are employed^{1,4-6}. To increase the rate and facilitate complete reaction, various catalysts, such as I_2 ⁵, CCl_4 ⁶, allyl iodide⁷ and MgI_2 ⁸ are used. Intimate mixing of $LaNi_5$ ⁹, Mg_2Cu ¹⁰ or Fe¹¹ with Mg metal decreases the time needed to complete hydride formation; e.g., the addition of 20% $LaNi_5$ increases the percentage completion after 15 min (at 345°C) from ca. 12% for pure Mg, to over 80% for the mixture⁹. These latter three catalysts provide an oxide-free surface¹⁰ to facilitate dissociative adsorption of the H_2 .

The addition of about 1% (or less) of a group III metal, such as Al, Ge or In, to the Mg increases the hydride-formation rate¹².

Homogeneous catalysts via the action of anthracene Mg in tetrahydrofuran (THF)¹² with Cr, Ti or Fe halides in THF allow the complete formation of MgH_2 in ca. 10 h at 8 MPa and only 60–70°C.

Magnesium powder of small particle size can be hydrided completely and rapidly without the use of a catalyst; e.g., under 3.5 MPa of H_2 complete conversion to MgH_2 occurs¹⁴ within 15 min at 400°C, provided the particle size is < 100 μm .

Under high hydrostatic P (8000 MPa) and 800°C, normal MgH_2 , in which the coordination number for Mg is six, is converted to a phase of higher density, in which the Mg has eight nearest-neighbor H atoms¹⁵.

(G.G. LIBOWITZ)

1. E. Wiberg, R. Bauer, *Chem. Ber.*, **85**, 593 (1952).
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1.8.3.3. Calcium, Strontium and Barium Hydrides

The hydrides of Ca, Sr and Ba are formed by direct reaction of the metal and H_2 at elevated T (see §1.12.1).

158 1.8. Formation of Bonds between Hydrogen and Group IA or IIA Metals

1.8.3. Alkaline-Earth Metal Hydrides

Direct reaction of Mg and H_2 at elevated T and P yields MgH_2 . The rate is slow, and the process is difficult to carry to completion because the metal particles become coated with a dense layer of the hydride, through which the H_2 must diffuse. If the T is raised to increase the diffusion rate, the dissociation P is also increased and, for the reaction to proceed, the ambient H_2 P must exceed the dissociation P; e.g., 40 MPa and over 500°C are employed^{1,4-6}. To increase the rate and facilitate complete reaction, various catalysts, such as I_2 ⁵, CCl_4 ⁶, allyl iodide⁷ and MgI_2 ⁸ are used. Intimate mixing of $LaNi_5$ ⁹, Mg_2Cu ¹⁰ or Fe¹¹ with Mg metal decreases the time needed to complete hydride formation; e.g., the addition of 20% $LaNi_5$ increases the percentage completion after 15 min (at 345°C) from ca. 12% for pure Mg, to over 80% for the mixture⁹. These latter three catalysts provide an oxide-free surface¹⁰ to facilitate dissociative adsorption of the H_2 .

The addition of about 1% (or less) of a group III metal, such as Al, Ge or In, to the Mg increases the hydride-formation rate¹².

Homogeneous catalysts via the action of anthracene Mg in tetrahydrofuran (THF)¹² with Cr, Ti or Fe halides in THF allow the complete formation of MgH_2 in ca. 10 h at 8 MPa and only 60–70°C.

Magnesium powder of small particle size can be hydrided completely and rapidly without the use of a catalyst; e.g., under 3.5 MPa of H_2 complete conversion to MgH_2 occurs¹⁴ within 15 min at 400°C, provided the particle size is < 100 μm .

Under high hydrostatic P (8000 MPa) and 800°C, normal MgH_2 , in which the coordination number for Mg is six, is converted to a phase of higher density, in which the Mg has eight nearest-neighbor H atoms¹⁵.

(G.G. LIBOWITZ)

1. E. Wiberg, R. Bauer, *Chem. Ber.*, **85**, 593 (1952).
2. G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Nilzbach, H. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 4585 (1951).
3. M. Givélet, *C.R. Hebd. Seances Acad. Sci.*, **267**, 881 (1968).
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Because these metals are reactive with air and moisture, care must be taken to prevent oxidation, which would impede hydride formation. For the formation of CaH_2 , 300–350°C is optimum¹. Formation of SrH_2 and BaH_2 occurs² at elevated T. These hydrides react violently with H_2O , as do the alkali-metal hydrides.

(G.G. LIBOWITZ)

1. C. E. Messer, *Prep. Inorg. React.*, 1, 203 (1964).

2. A. F. Zhigach, D. S. Stasinevitch, *Chemistry of Hydrides*, Khimiya, Leningrad, 1969.

1.9. Formation of Bonds between Hydrogen and Metals of Group IB (Cu, Ag, Au) or IIB (Zn, Cd, Hg)

1.9.1. Introduction

The reaction of transition metals with H_2 is distinct from the physical diffusion of H_2 through the solid metal. The group IB metals give no evidence of hydride formation, although they are important in the reaction¹⁻³ of alloys such as Pd-Cu and Pd-Ag with H_2 .

There are many examples of borohydride compounds of these metals, e.g., Cu, Ag, Zn and $Cd-BH_4$ as neutral and anionic complexes in which the mode of bonding of BH_4 is dependent on the coordination number of the metal⁴. Higher borane anions also combine with Cu and Ag, yielding both neutral and anionic complexes. Although no borohydrides of Au are isolated, treatment of Au-halide complexes with, e.g., $NaBH_4$, is a standard method for the preparation of Au-cluster compounds⁵. Copper(I) hydride, first reported⁶ in 1844, has the ZnS structure⁷ [$d(Cu-H) = 0.173$ nm (1.73 \AA); $d(Cu-Cu) = 0.289$ nm (2.89 \AA)] and decomposes to the elements when heated. At $\geq 100^\circ C$ the decomposition is explosive.

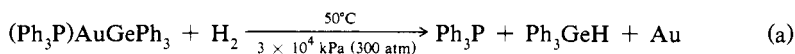
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Hydrogen gas diffuses through Cu at above $450^\circ C$, provided the metal is oxygen-free, the rate being proportional to $(P_{H_2})^{1/2}$, but CuH is not established under these conditions¹. In the vapor phase at $1400^\circ C$, however, Cu and H_2 form² CuH.

The formation of Ag(I) and Au(I) hydrides at $> 1000^\circ C$ in H_2 is confirmed by spectroscopic studies on the metal hydrides and deuterides in the vapor phase³. Attempts to prepare an Au hydride-phosphine complex from H_2 in solution fail, although one is almost certainly formed as an intermediate⁴:



When the intermetallic alloy $CaAg_2$ is heated in H_2 at $575-600^\circ C$ for 16-18 h, the

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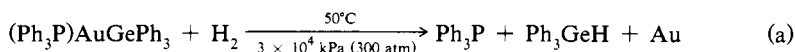
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Atomic hydrogen in the presence of Cu gives^{1,2} a black Cu(I) hydride at low T. If an electric discharge is passed between Ag electrodes in the presence of H_2 , AgH can be identified spectroscopically.

The reaction of metals with energetic hydrogen or deuterium ions is important in nuclear reactors. Ion beams may be generated thermally and allowed to interact with the metal, and the reaction products then may be examined by matrix-isolation techniques. Alternatively, metal atoms are sputtered from a cathodic surface by a low-energy plasma. If H_2 or D_2 at low P is added to the discharge, then molecular species are formed by the interaction with the sputtered metal atoms. Applied to Cu this technique leads to the identification of CuH and CuD in Ar matrices by their IR spectra. The reacting species are believed to be atomic Cu and H or D formed in the hollow-cathode discharge³.

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Alkali-metal hydrides are not used as a route to group IB-metal hydrides; complex metal hydrides are used instead.

(F. GLOCKLING)

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This is the best method for preparing Zn dihydride, because using equimol ratios of NaH and ZnCl_2 or LiH and ZnBr_2 gives Zn dihydride free from anionic species. Sodium hydride and ZnI_2 in a 2:1 ratio also give ZnH_2 , but if the ratio of alkali-metal hydride to ZnX_2 is increased, then the ZnH_2 is contaminated with complex hydrides^{1,2}.

1.9. Formation of Bonds between Hydrogen and Cu, Ag, Au or Zn, Cd, Hg 161

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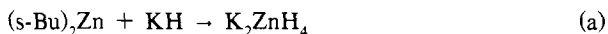
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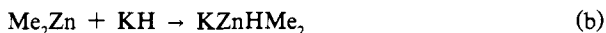
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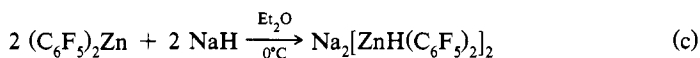
Zinc dialkyls are also reduced by alkali-metal hydrides; the products depend on the alkyl group and on the ratio of reactants. Di(s-butyl)zinc and KH yield an anionic hydride:



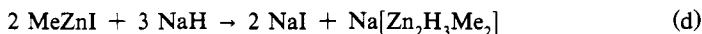
By contrast, dimethylzinc gives first a monohydride anion, which is insoluble in ether but dissolves in THF:



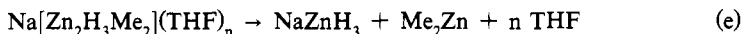
Reaction of KZnHMe_2 with a further mol of Me_2Zn yields the unstable complex, $\text{K}[\text{Zn}_2\text{HMe}_4]$. Related arylzinc hydrides (and deuterides) such as $\text{Na}[\text{ZnHPh}_2]$ are prepared in the same way. The product from $(\text{C}_6\text{F}_5)_2\text{Zn}$ and NaH is ether soluble:



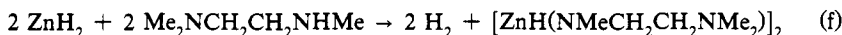
and on the basis of IR and mol wt measurements has a double hydrogen-bridged structure. Reduction of methylzinc iodide with Na hydride produces a mixed dimeric alkyl hydride:



Anion structures with single- or triple-hydrogen bridges are proposed. It decomposes at $\geq \text{RT}$ in vacuo to NaZnH_3 , which has greater thermal stability but is rapidly hydrolyzed³:



A neutral dimeric Zn-hydride complex is isolated as a white, crystalline solid having terminal rather than bridging Zn—H bonds⁴:



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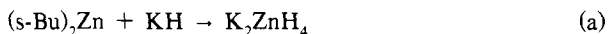
Copper(I) chloride reacts with AlH_3 in ether at -78°C , and on the basis of elemental analysis and IR spectra, it appears that the reaction up to RT is:



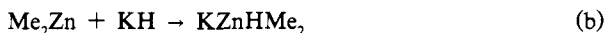
In the absence of strongly π -bonding ligands such as tertiary phosphines, complex hydrides, e.g., $[\text{AlH}_4]^-$ and $[\text{BH}_4]^-$ react with Cu, Ag and Au halides to form metal-hydrogen compounds, usually of low thermal stability. Uncomplexed CuH is unstable, even at -80°C .

162 1.9. Formation of Bonds between Hydrogen and Cu, Ag, Au or Zn, Cd, Hg

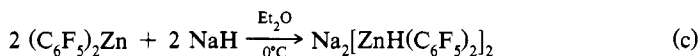
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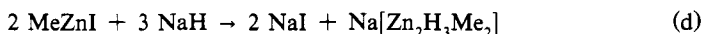
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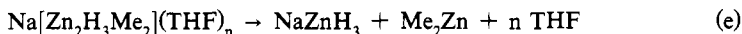
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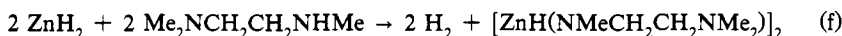
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1.9.5. by Neutral and Anionic Metal Hydride Reduction

1.9.5.1. of Compounds of Group IB.

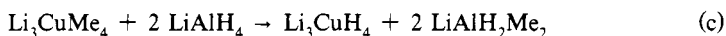
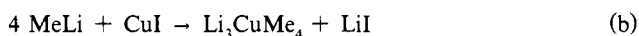
Copper(I) chloride reacts with AlH_3 in ether at -78°C , and on the basis of elemental analysis and IR spectra, it appears that the reaction up to RT is:



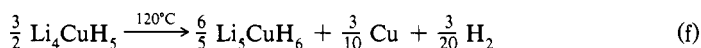
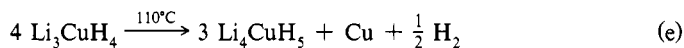
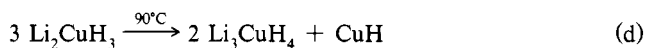
In the absence of strongly π -bonding ligands such as tertiary phosphines, complex hydrides, e.g., $[\text{AlH}_4]^-$ and $[\text{BH}_4]^-$ react with Cu, Ag and Au halides to form metal-hydrogen compounds, usually of low thermal stability. Uncomplexed CuH is unstable, even at -80°C .

When LiAlH_4 is added to Cu(I) iodide in pyridine, a red-brown powder separates on addition of ether. This solid contains Cu(I) hydride together with LiI , CuI and pyridine, which stabilize it¹.

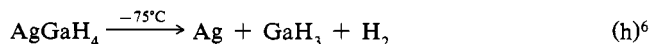
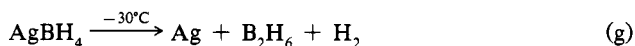
When $\text{Li}[\text{CuMe}_2]$ reacts with metal boro- or almino-hydrides, complex hydrides of Cu are formed. Although not fully characterized, these can be formulated² as MCuH_2 . Similarly, reduction of CuI by $\text{K}[\text{n-Bu}_3\text{BH}]$ yields³ KCuH_2 . By varying the experimental conditions, the reduction of LiCuMe_2 with LiAlH_4 yields a range of anionic Cu hydrides (e.g., LiCuH_2 , Li_2CuH_3 , Li_3CuH_4 , Li_4CuH_5 , Li_6CuH_6). In addition, this reaction leads to salts with more than one Cu atom in the anion (e.g., LiCu_2H_3 , $\text{Li}_2\text{Cu}_3\text{H}_5$). Most of these complexes have transitory stability at RT; e.g., LiCuH_2 is stable at 0°C for several weeks. These hydrides are almost certainly formed by $[\text{AlH}_4]^-$ reduction of the preformed methylcopper anion, e.g.:



These complexes are unsolvated. Their thermal decomposition by differential-thermal and thermal-gravimetric analyses (DTA and TGA) provides evidence for the conversion of one hydride complex into another with partial loss of Cu and H_2 , e.g.:

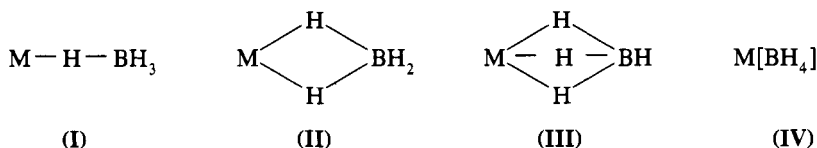


With Ag no binary hydride is known, but several thermally unstable complex hydrides are isolated that contain H bonded to Ag. For example, LiAlH_4 , LiBH_4 or LiGaH_4 react with Ag perchlorate in ether to give white or yellow precipitates of AgAlH_4 , AgBH_4 and AgGaH_4 . Thermal decomposition occurs below RT and is catalyzed⁵ by Ag:



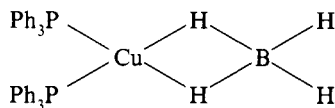
Gold(III) also forms complex hydrides with LiAlH_4 and LiBH_4 , stable only at low T. Analyses of the precipitated solids lead to such compositions as $\text{Al}_6\text{Au}_2\text{H}_{24}$, of unknown structure⁷.

Stable molecular borohydride complexes of Cu, and to a lesser extent Ag and Au, are isolated, and each of the four possible bonding modes (I–IV) is identified⁸:



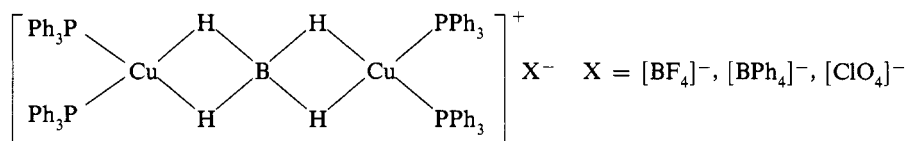
When Na borohydride in ethanol is added to Cu(I) chloride containing an electron-pair donor, reaction occurs at RT, with its course determined by the steric and

donor-acceptor properties of the base. For triarylphosphines the reaction gives stable borohydride complexes such as $(\text{Ph}_3\text{P})_2\text{Cu}(\text{BH}_4)$. With trialkylphosphines, Ph_3As , Ph_3Sb , or the sterically hindered tri-*o*-tolylphosphine, H_2 evolves and Cu is precipitated. The chelating diphosphine $(\text{Ph}_2\text{PCH}_2)_2$ (dppe) also yields a stable complex, $(\text{dppe})\text{Cu}(\text{BH}_4)$. Bis(triphenylphosphine)copper(I) borohydride is a crystalline complex in which both Cu and boron have a quasi-tetrahedral configuration (V):



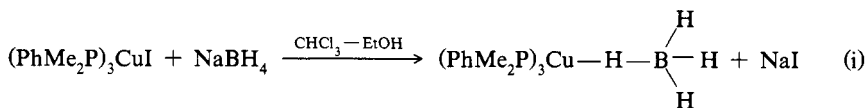
(V)

The deuterium analogue of (I) is also known^{9,10}. When $(\text{Ph}_3\text{P})_2\text{CuBH}_4$ is treated with HClO_4 in ethanol a soluble complex is first produced, which with more HClO_4 yields $[(\text{Ph}_3\text{P})_2\text{CuClO}_4]_2$. The soluble complex, $[(\text{Ph}_3\text{P})_4\text{Cu}_2\text{BH}_4]\text{ClO}_4$, is a white, diamagnetic solid; IR evidence suggests the structure¹¹ (VI):

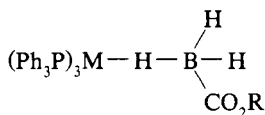


(VI)

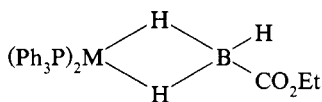
Substitution reactions in which halide ion is displaced by $[\text{BH}_4]^-$ are also dependent on the halide; e.g., whereas neither $(\text{Ph}_2\text{MeP})_3\text{CuI}$ nor $(\text{PhMe}_2\text{P})_3\text{CuI}$ reacts with $[\text{BH}_4]^-$ at RT, reaction with the corresponding chloro complexes is rapid and quantitative. For both phosphines, a single $\text{Cu}-\text{H}-\text{B}$ bridged structure results¹² with four-coordinated Cu:



Substituted borohydrides, $[\text{BH}_3\text{X}]^-$, are used to form Cu and Ag complexes¹⁵. The anion $[\text{H}_3\text{BCO}_2\text{R}]^-$ reacts with triphenylphosphine complexes of Cu(I) and Ag(I) in chloroform-ethanol, yielding $(\text{Ph}_3\text{P})_n\text{MH}_3\text{BCO}_2\text{R}$ (where $n = 2, 3$ and $\text{R} = \text{H}, \text{Me}, \text{Et}$). If 3 mol of phosphine are coordinated to Cu or Ag, structure (VII) results, whereas in complexes with 2 mol of triphenylphosphine, two hydrogen bridges are formed (VIII):



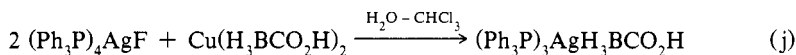
(VII)



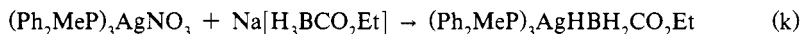
(VIII)

The structural evidence for these two forms of bonding comes from IR and NMR data¹³.

Monodentate bonding is confirmed for $(\text{Ph}_2\text{MeP})_3\text{CuBH}_4$ by crystallography¹⁴. The Ag complex $(\text{Ph}_3\text{P})_3\text{AgH}_3\text{BCO}_2\text{R}$ can also be obtained from:

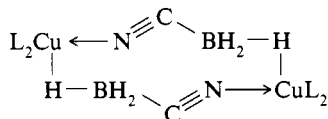


Silver nitrate–phosphine complexes are used to prepare borane derivatives¹²:



The extent of neutral ligand dissociation follows the order: $\text{L}_3\text{CuBH}_4 > \text{L}_3\text{AgBH}_4 \geq \text{L}_3\text{AgH}_3\text{BCO}_2\text{Et} > \text{L}_3\text{CuH}_3\text{BCO}_2\text{Et}$.

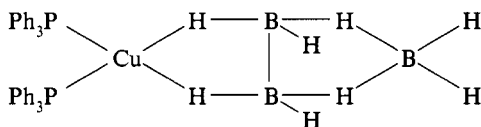
The isocyanotrihydroborate ion, $[\text{NCBH}_3]^-$, coordinates to transition metals through nitrogen, and likewise with Cu(I), giving, e.g., $(\text{Ph}_3\text{P})_3\text{Cu}(\text{NCBH}_3)$ which is weakly conducting in acetonitrile (Ag analogues of lower stability are also obtained). However, complexes with only two neutral ligands have different IR spectra, consistent with a hydrogen-bridged dimer (IX)¹⁶, from a crystal structure¹⁷ of $(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBH}_3)_2$.



(IX)

A hydridocopper cluster is isolated as red, hexagonal plates from the reaction between $(\text{Ph}_3\text{PCuCl})_4$ and Na trimethoxyborohydride in dimethylformamide (DMF). The reaction takes place over 30 min at RT yielding $\text{Cu}_6\text{H}_6(\text{PPh}_3)_6 \cdot \text{DMF}$ as a thermally stable solid that slowly oxidizes in air. X-Ray diffraction shows that the Cu_6 cluster is distorted from regular O_h symmetry, and that one Ph_3P molecule is bonded to each Cu atom. The positions of the hydrogen atoms are not known nor are they detected by IR or ^1H NMR spectroscopy; their presence is demonstrated by decomposition of the complex using PhCO_2D when HD and H_2 are formed, but not D_2 . Moreover, the geometry of the skeleton [(a) and (b), Fig. 1] precludes the possibility of terminal Cu—H bonding and hence suggests that the six hydrogen atoms either bridge each edge of the large (or small) triangular faces or form triple bridges to the triangular faces. Assuming that the Ph_3P and H^- ligands each contribute two electrons, then this cluster has a noble-gas configuration¹⁸.

Formation of Cu(I) borohydride complexes with bridging H at is not limited to the $[\text{BH}_4]^-$ ion; if $(\text{Ph}_3\text{P})_2\text{CuCl}$ is treated with $\text{Cs}[\text{B}_3\text{H}_8]$ in acetone the crystalline complex $(\text{Ph}_3\text{P})_2\text{CuB}_3\text{H}_8$ is isolated. A similar procedure leads to the triphenylarsine and -stibine analogues. The structure (XII) of solid $(\text{Ph}_3\text{P})_2\text{Cu}(\text{B}_3\text{H}_8)$ is:



(XII)

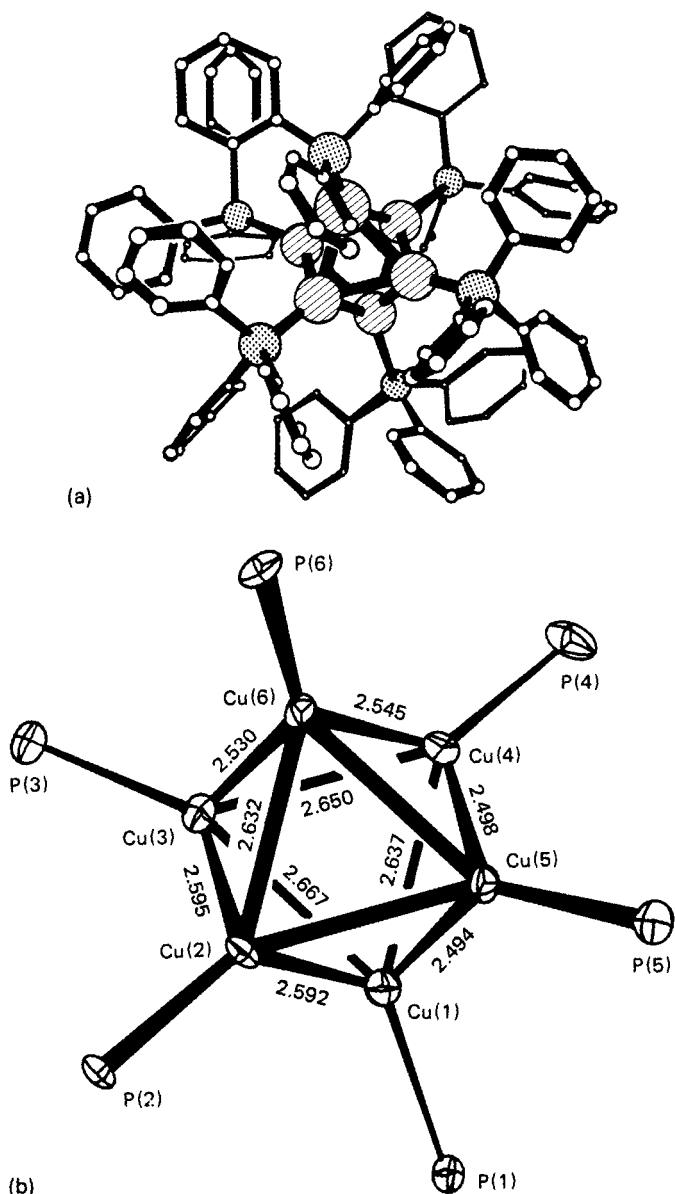
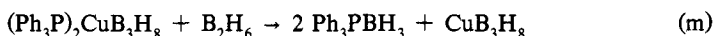
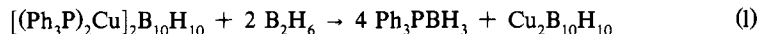


Figure 1. (a) Stereochemistry of $\text{H}_6\text{Cu}_6(\text{PPh}_3)_6$. (b) Cu-Cu distances within the $\text{H}_6\text{Cu}_6(\text{PPh}_3)_6$ cluster. Reproduced by permission of the authors and the Editor of the *Journal of the American Chemical Society*.

In solution it is monomeric and a nonelectrolyte, and its structure involves bonding between Cu and terminal protons on two different boron atoms. In this and related complexes with two Ph_3As or $(\text{PhO})_3\text{P}$ ligands bonded¹⁹ to Cu, variable-T NMR studies show that the $[\text{B}_3\text{H}_8]^-$ ion rearranges, and that the activation energy for this scrambling or fluxional behavior depends on the effective positive charge on Cu: the greater the positive charge, the stronger the binding to $[\text{B}_3\text{H}_8]^-$.

In $(\text{Ph}_3\text{P})_2\text{CuB}_3\text{H}_8$ the phosphine ligands are also labile (by ^{31}P NMR), and the labile Ph_3P molecules can be captured by the addition of B_2H_6 to Cu(I)-borane complexes²⁰:

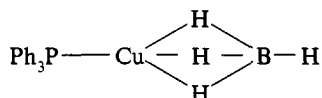


The polymeric borane CuB_3H_8 is stable at RT in the absence of air; it is suggested that each Cu atom is bonded to more than one B_3H_8 unit through Cu—H—B bridges.

The capture of labile Ph_3P from $(\text{Ph}_3\text{P})_2\text{CuB}_3\text{H}_8$ can be taken to the halfway stage:



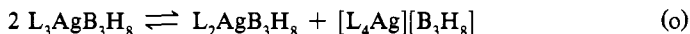
Attempts to precipitate $\text{Ph}_3\text{PCuB}_3\text{H}_8$ fail because of its redistribution to $(\text{Ph}_3\text{P})_2\text{CuB}_3\text{H}_8$ and CuB_3H_8 . In a similar reaction one mol of Ph_3P may be removed from $(\text{Ph}_3\text{P})_2\text{CuBH}_4$, yielding $(\text{Ph}_3\text{P})\text{CuBH}_4$, but this also is too unstable to isolate the solid. Its structure, based on vibrational and NMR spectroscopy, is consistent with a triple Cu—H—B bridge and four-coordinated Cu(I):



(XIII)

At above -20°C $\text{Ph}_3\text{PCuBH}_4$ decomposes to a black solid, believed to be CuH, together with Ph_3PBH_3 .

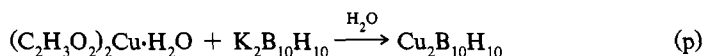
Triphosphine silver complexes (L=phosphine) with $[\text{B}_3\text{H}_8]^-$ disproportionate:



Gold(I) complexes form only $[\text{L}_4\text{Au}][\text{borane}]$ salts on reaction with anionic boranes.

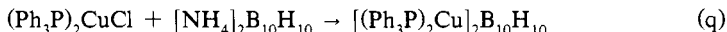
Copper and Ag complexes of the higher boranes are prepared by reaction of the metal-halide complex with a borane anion, including²¹⁻²³, B_3H_8 , B_6H_9 , $\text{B}_9\text{H}_{12}\text{S}$, B_9H_{14} , $\text{B}_{10}\text{H}_{13}$ and $\text{B}_{11}\text{H}_{14}$. Pentaborane(9) and hexaborane(10) form the Cu complexes $(\text{Ph}_3\text{P})_2\text{CuB}_5\text{H}_8$ and $(\text{Ph}_3\text{P})_2\text{CuB}_6\text{H}_9$; both are white, air-stable solids, formed in THF- CH_2Cl_2 from which they are precipitated by ether²⁴.

Most compounds have neutral (group VA or VIA) ligands bonded to Cu, but CuCl_2 and $[\text{B}_{10}\text{H}_{13}]^{2-}$ yield the complex, $(\text{Et}_4\text{N})_2(\text{Cl}_2\text{CuB}_{10}\text{H}_{13})$. With $[\text{B}_9\text{H}_{14}]^-$, $[\text{B}_9\text{H}_{12}\text{S}]^-$ and $[\text{B}_{11}\text{H}_{14}]^-$ only ionic tetrakis(triphenylphosphine)Cu and -Ag salts are isolated. The decaborane $\text{Cu}_{12}\text{B}_{10}\text{H}_{10}$ is also prepared by:



and separates as white crystals from acetonitrile. The corresponding deuteride is also known. X-Ray diffraction gives the geometry without revealing the positions of the H atoms; comparison of its IR spectrum and that of $\text{Cu}_2\text{B}_{10}\text{D}_{10}$ with the free ion $[\text{B}_{10}\text{H}_{10}]^{2-}$ suggests that the terminal $\text{B}_{10}\text{H}_{10}$ hydrogen atoms are involved in forming three-center $\text{Cu}-\text{H}-\text{B}$ bridge bonds, making the Cu(I) atoms sp^3 hybridized².

Bridge $\text{Cu}-\text{H}-\text{B}$ bonding is present in $[(\text{Ph}_3\text{P})_2\text{Cu}]_2\text{B}_{10}\text{H}_{10}$ from solid-state studies, and solution IR studies also favor this view. The complex is made by the direct reaction^{25,26}:



The pentaborane-Cu(I) complex $(\text{Ph}_3\text{P})_2\text{CuB}_5\text{H}_8$ has the Cu atom bonded to a basal boron-site; it is nonfluxional and is prepared by standard techniques. The tendency toward coordination to Cu follows: $\text{B}_3\text{H}_8 > \text{B}_{10}\text{H}_{13} > \text{B}_9\text{H}_{12}\text{S} > \text{B}_9\text{H}_{14} \approx \text{B}_{11}\text{H}_{14}$.

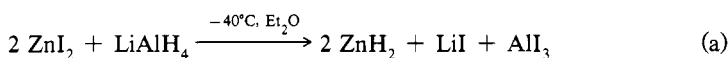
(F. GLOCKLING)

1. J. A. Dilts, D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 5789 (1968).
2. E. C. Ashby, T. F. Korenowski, R. D. Schwarz, *J. Chem. Soc., Chem. Commun.*, 157 (1974).
3. T. Yoshida, E. Negishi, *J. Chem. Soc., Chem. Commun.*, 762 (1974).
4. E. C. Ashby, A. B. Goel, *Inorg. Chem.*, **16**, 3043 (1977).
5. E. Wiberg, W. Henle, *Z. Naturforsch., Teil B*, **76**, 250, 575, 576 (1952).
6. J. P. Chan, R. Hultgren, *J. Chem. Thermodyn.*, **1**, 45 (1969).
7. E. Wiberg, H. Neumauer, *Inorg. Nucl. Chem. Lett.*, **1**, 35 (1965).
8. S. J. Lippard, D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).
9. F. Cariati, L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).
10. S. J. Lippard, K. M. Melmed, *J. Am. Chem. Soc.*, **89**, 3929 (1967).
11. F. Cariati, L. Naldini, *J. Inorg. Nucl. Chem.*, **28**, 2243 (1966).
12. J. C. Bommer, K. W. Morse, *Inorg. Chem.*, **19**, 587, (1980).
13. J. C. Bommer, K. W. Morse, *Inorg. Chem.*, **18**, 531 (1979).
14. C. Kotal, P. Grutsch, J. L. Atwood, R. D. Rogers, *Inorg. Chem.*, **17**, 3558 (1978).
15. J. C. Bommer, K. W. Morse, *J. Am. Chem. Soc.*, **96**, 6222 (1974).
16. S. J. Lippard, P. S. Welcker, *Inorg. Chem.*, **11**, 6 (1972).
17. K. M. Melmed, T. Li, J. J. Mayerle, S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 69 (1974).
18. S. A. Bezman, M. R. Churchill, J. A. Osborn, J. Wormald, *J. Am. Chem. Soc.*, **93**, 2063 (1971).
19. C. H. Bushweller, H. Beall, W. J. Dewkett, *Inorg. Chem.*, **15**, 1739 (1976).
20. R. K. Hertz, R. Goetze, S. G. Shore, *Inorg. Chem.*, **18**, 2813 (1979).
21. F. Clanberg, E. L. Muetterties, L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).
22. E. L. Muetterties, W. G. Peet, P. A. Wegner, C. W. Abgranti, *Inorg. Chem.*, **9**, 2447 (1970).
23. V. T. Brice, S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1312 (1970).
24. T. E. Paxson, M. F. Hawthorne, L. D. Brown, *Inorg. Chem.*, **13**, 2772 (1974).
25. J. T. Gill, S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
26. G. G. Outterson, V. T. Brice, S. G. Shore, *Inorg. Chem.*, **15**, 1456 (1976).

1.9.5.2. of Compounds of Group IIB.

Although Hg hydrides are claimed, most studies relate to Zn and Cd, where polymeric binary compounds, $(\text{MH}_2)_n$, are isolated as well as anionic metal hydrides, e.g., LiZnH_3 , Li_2ZnH_4 , Li_3ZnH_5 . In addition, borohydride complexes such as $\text{Cd}(\text{BH}_4)_2 \cdot \text{THF}$ are reported, some having more than one metal atom in the anion.

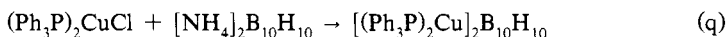
A white, solid, polymeric Zn dihydride is made by the action of LiAl hydride on Zn iodide or dimethylzinc:



168 1.9. Formation of Bonds between Hydrogen and Cu, Ag, Au or Zn, Cd, Hg
1.9.5. by Neutral and Anionic Metal Hydride Reduction

and separates as white crystals from acetonitrile. The corresponding deuteride is also known. X-Ray diffraction gives the geometry without revealing the positions of the H atoms; comparison of its IR spectrum and that of $\text{Cu}_2\text{B}_{10}\text{D}_{10}$ with the free ion $[\text{B}_{10}\text{H}_{10}]^{2-}$ suggests that the terminal $\text{B}_{10}\text{H}_{10}$ hydrogen atoms are involved in forming three-center $\text{Cu}-\text{H}-\text{B}$ bridge bonds, making the Cu(I) atoms sp^3 hybridized².

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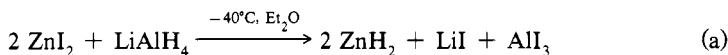
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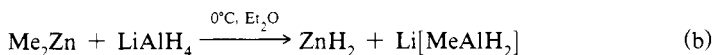
1. J. A. Dilts, D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 5789 (1968).
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14. C. Kutal, P. Grutsch, J. L. Atwood, R. D. Rogers, *Inorg. Chem.*, **17**, 3558 (1978).
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19. C. H. Bushweller, H. Beall, W. J. Dewkett, *Inorg. Chem.*, **15**, 1739 (1976).
20. R. K. Hertz, R. Goetze, S. G. Shore, *Inorg. Chem.*, **18**, 2813 (1979).
21. F. Clanberg, E. L. Muetterties, L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968).
22. E. L. Muetterties, W. G. Peet, P. A. Wegner, C. W. Abgranti, *Inorg. Chem.*, **9**, 2447 (1970).
23. V. T. Brice, S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 1312 (1970).
24. T. E. Paxson, M. F. Hawthorne, L. D. Brown, *Inorg. Chem.*, **13**, 2772 (1974).
25. J. T. Gill, S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
26. G. G. Outtersen, V. T. Brice, S. G. Shore, *Inorg. Chem.*, **15**, 1456 (1976).

1.9.5.2. of Compounds of Group IIB.

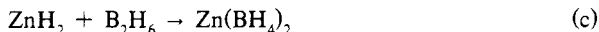
Although Hg hydrides are claimed, most studies relate to Zn and Cd, where polymeric binary compounds, $(\text{MH}_2)_n$, are isolated as well as anionic metal hydrides, e.g., LiZnH_3 , Li_2ZnH_4 , Li_3ZnH_5 . In addition, borohydride complexes such as $\text{Cd}(\text{BH}_4)_2 \cdot \text{THF}$ are reported, some having more than one metal atom in the anion.

A white, solid, polymeric Zn dihydride is made by the action of LiAl hydride on Zn iodide or dimethylzinc:





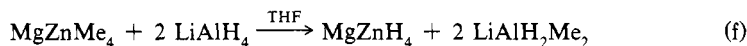
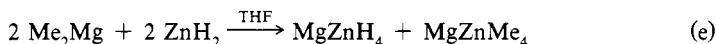
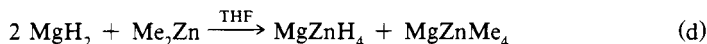
This polymeric Zn dihydride is converted into the borohydride by reaction with diborane:



Cadmium dihydride, which is also polymeric, is prepared by the same methods¹⁻³ and HgH_2 is claimed from the reaction of HgI_2 with LiAlH_4 at low T.

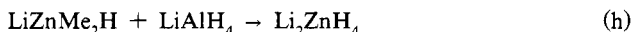
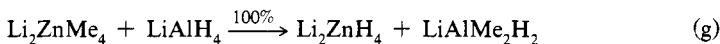
Aluminium hydride reacts with anhyd Zn chloride or bromide to give a polymeric complex, $\text{Zn}_2\text{H}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$), whereas Zn iodide gives an insoluble product, ZnI_2AlH_3 . Under similar conditions CdBr_2 reacts⁴ slowly to yield CdHBr . Structural information is limited to IR spectra because of their low solubility and reluctance to form crystals.

Complex Zn hydrides are isolated by procedures that are variations on earlier methods⁵⁻⁷:

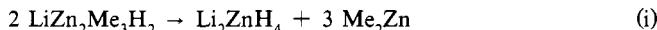


The complex MgZnH_4 forms a white, insoluble solid with two mol of THF, leaving the metal-methyl complex in solution.

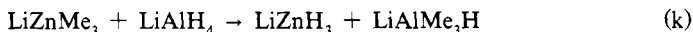
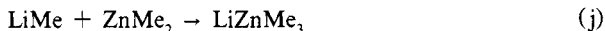
Alkylzinc complexes including LiZnMe_3 and Li_2ZnMe_4 are reduced^{6,7} with LiAlH_4 , NaAlH_4 and AlH_3 . These reactions, which yield complex hydrides of zinc, proceed in high yield, without the complications that result from ether-cleavage side reactions:



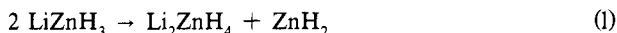
Although these reactions proceed rapidly, $\text{LiZn}_2\text{Me}_3\text{H}$ reacts with LiAlH_4 slowly, requiring five days. The reaction involves a slow exchange of a methyl group from $\text{LiZn}_2\text{Me}_4\text{H}$ to yield the intermediate $\text{LiZn}_2\text{Me}_3\text{H}_2$ which then disproportionates:



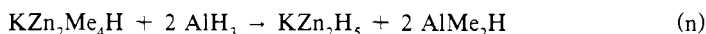
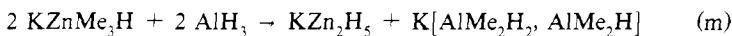
The reduction of Li_3ZnMe_5 with LiAlH_4 in diethyl ether at RT gives Li_3ZnH_5 quantitatively. This complex is not a physical mixture of $\text{Li}_3\text{ZnH}_4 + \text{LiH}$, but its insolubility limits structural studies. Similar limitations apply to LiZnH_3 , formed by:



Its thermal decomposition to $\text{Li} + \text{Zn} + \text{H}_2$ proceeds through a disproportionation step:

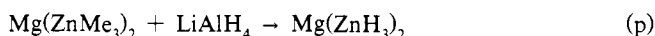
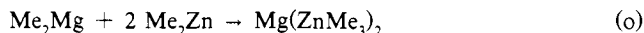


X-ray powder diffraction demonstrates that complexes with the stoichiometry LiZn_2H_5 and LiZn_3H_7 are physical mixtures of LiZnH_3 and ZnH_2 . However, the reaction between KZnMe_2H or $\text{KZn}_2\text{Me}_4\text{H}$ and Al hydride in THF proceeds according to:



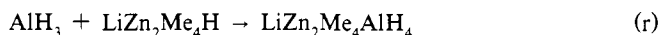
X-Ray studies suggest that KZn_2H_5 is a genuine hydride complex; it decomposes thermally to $\text{Zn} + \text{K} + \text{H}_2$ via KZnH_3 and K_2ZnH_4 . Changing the stoichiometry in the AlH_3 reaction leads to a solid having the composition KZn_3H_7 , but this, like the lithium analogue, is a mixture of ZnH_2 and KZn_2H_5 .

The complex $\text{Mg}(\text{ZnH}_3)_2 \cdot 0.5 \text{Et}_2\text{O}$ is obtained by:

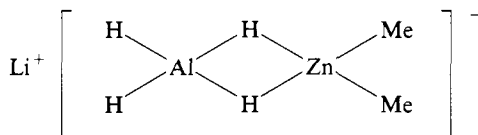


X-Ray powder examination shows that it is not a physical mixture of MgH_2 and ZnH_2 , although when heated its thermal decomposition proceeds via dissociation into $\text{MgH}_2 + 2 \text{ZnH}_2$ after initial loss of ether.

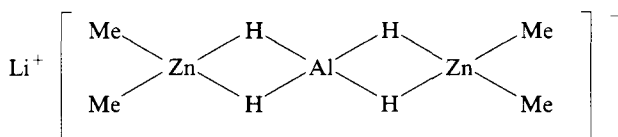
Aluminum hydride and Li methylzinc hydrides form a further series of complexes:



Spectroscopic data suggest structures (I) and (II):

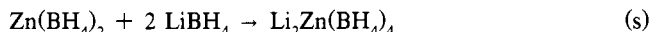


(I)

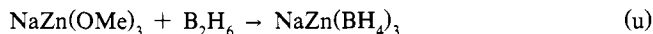
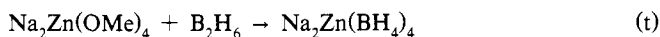


(II)

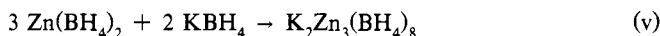
The borane complex, $[\text{NaOEt}_2][\text{Zn}(\text{BH}_4)_3]$, formed⁸ by reaction of xs NaBH_4 on ZnCl_2 in ether is stable to 80°C . Anionic complexes are synthesized^{9,10}:

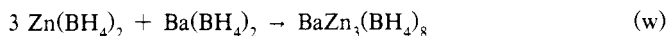


Other starting materials may be used to give anionic-borane complexes:



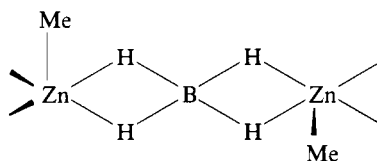
Surprisingly, the nature of the isolated product depends on the cation, and trimetallic borohydride ions are obtained:





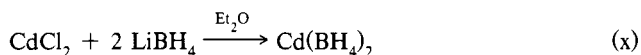
Infrared and ^{11}B NMR evidence suggests the presence of ZnH_2BH_2 units with eight-coordinated Zn in the $[\text{Zn}(\text{BH}_4)_4]^{2-}$ anion.

The cleavage of dimethylzinc by borohydride can also yield the unsymmetrical compound¹¹, MeZnBH_4 . Its IR spectrum shows a five-coordinated zinc polymer with $\text{ZnH}_2\text{BH}_2\text{Zn}$ units:



(III)

Impure cadmium bis(tetrahydroborate), $\text{Cd}(\text{BH}_4)_2$, is obtained by:



It decomposes at ca. 25°C and is air sensitive¹². The main product is the complex salt, $\text{Li}_2[\text{Cd}(\text{BH}_4)_4]$, isolated as an oily etherate. The analogous reaction using Na borohydride also yields a complex salt, $\text{Na}[\text{Cd}(\text{BH}_4)_3]$.

Neutral Cd borohydride complexes analogous to those of Zn also are isolated and are more thermally stable than $\text{Cd}(\text{BH}_4)_2$:



Pyridine or NH_3 may take the place of THF in these complexes¹²⁻¹³.

Both Zn and Cd dimethyls (but not Me_2Hg) react with hexaborane(10) at 0°C liberating methane. From the Zn reaction the complex $\text{Zn}(\text{THF})_2(\text{B}_6\text{H}_9)_2$ is isolated as a white solid, whereas the Cd analogue contains only a little coordinated THF. Both compounds are stereochemically nonrigid by ^1H NMR spectroscopy, with both the metal and bridging hydrogen atoms involved in the dynamic processes. However, at low T their structures result from insertion of Zn (or Cd) into a basal boron-boron bond in the anion¹³. Mercury carboranes are known, but their structures involve B—Hg—B bonding as in¹⁴ $\mu, \mu-(\text{Me}_2\text{B}_4\text{H}_5)_2\text{Hg}$.

(F. GLOCKLING)

1. G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, H. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 4585 (1951).
2. E. Wiberg, W. Henle, R. Bauer, *Z. Naturforsch., Teil B*, **6**, 393 (1957).
3. E. Wiberg, W. Henle, *Z. Naturforsch., Teil B*, **6**, 461 (1951).
4. E. C. Ashby, H. S. Prasad, *Inorg. Chem.*, **14**, 1608 (1975).
5. A. B. Gall, S. Gall, E. C. Ashby, *Inorg. Chem.*, **18**, 1433 (1969).
6. E. C. Ashby, K. C. Nainan, H. S. Prasad, *Inorg. Chem.*, **16**, 348 (1977).
7. E. C. Ashby, J. J. Watkins, *Inorg. Chem.*, **16**, 1445 (1977).
8. N. N. Maltseva, N. S. Kedrova, V. I. Mikleava, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **18**, 1054 (1973).
9. H. Nöth, E. Wiberg, L. P. Winter, *Z. Anorg. Allg. Chem.*, **386**, 73 (1971).

10. N. N. Maltseva, N. S. Kedrova, V. V. Klinkova, N. A. Chumakovski, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **20**, 339 (1975).
11. J. W. Nibler, T. H. Cook, *J. Chem. Phys.*, **58**, 1596 (1973).
12. H. Nöth, L. P. Winter, *Z. Anorg. Allg. Chem.*, **389**, 225 (1972).
13. D. L. Denton, W. R. Clayton, M. Mangion, S. G. Shore, E. A. Meyers, *Inorg. Chem.*, **15**, 541 (1976).
14. N. S. Hosmane, R. N. Grimes, *Inorg. Chem.*, **18**, 2886 (1979).

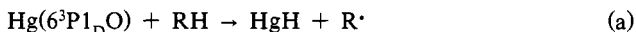
1.9.6. by Other Methods.

When CuSO_4 is treated with hypophosphorous acid, $\text{H}_2\text{P(O)OH}$, in H_2O a red-brown solid separates^{1,2} consisting mainly of CuH , although it also contains some Cu , Cu_2O and H_2O so that the ratio $\text{Cu}:\text{H}$ varies from 1:0.97 to 1:0.65. One of the advantages of this method is its simplicity, and by using deuteriohypophosphorous acid, the corresponding deuteride, CuD , may be obtained. Presumably, the impurities, including H_2O , stabilize Cu(I) hydride formed in this way.

Liquid NH_3 solns of CuI and an alkali-metal amide react with H_2 to give the solvated Cu hydride complexes³, $\text{K}_2\text{Cu}_3\text{H}_5(\text{NH}_3)_x$ and $\text{CsCuH}_2(\text{NH}_3)_x$.

The chemisorption of H_2 on Zn oxide is, in part, fast and reversible at RT, and this system involves both $\text{Zn}-\text{OH}$ and $\text{Zn}-\text{H}$ bonds (by IR), formed by the dissociation of H_2 (or D_2) on Zn oxide pair sites⁴.

Gas-phase HgH can be produced by the photosensitized decomposition of H_2 or alkanes⁵:



(F. GLOCKLING)

1. J. A. Goldkoop, A. F. Anderson, *Acta Crystallogr.*, **8**, 118 (1955).
2. J. C. Warf, W. Keitknecht, *Helv. Chim. Acta*, **33**, 613 (1950).
3. K. A. Strom, W. L. Jolly, *J. Inorg. Nucl. Chem.*, **35**, 3445 (1973).
4. C. C. Chang, R. Kokes, *J. Am. Chem. Soc.*, **93**, 7107 (1971).
5. A. G. Vikis, D. J. Le Roy, *Can. J. Chem.*, **50**, 595 (1972).

172 1.9. Formation of Bonds between Hydrogen and Cu, Ag, Au or Zn, Cd, Hg

-
10. N. N. Maltseva, N. S. Kedrova, V. V. Klinkova, N. A. Chumaevski, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **20**, 339 (1975).
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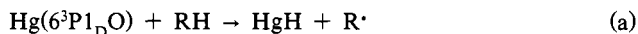
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3. K. A. Strom, W. L. Jolly, *J. Inorg. Nucl. Chem.*, **35**, 3445 (1973).
4. C. C. Chang, R. Kokes, *J. Am. Chem. Soc.*, **93**, 7107 (1971).
5. A. G. Vikis, D. J. Le Roy, *Can. J. Chem.*, **50**, 595 (1972).

1.10. Formation of Bonds between Hydrogen and Transition and Inner-Transition Metals

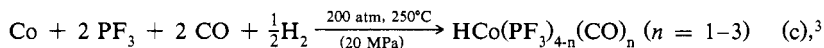
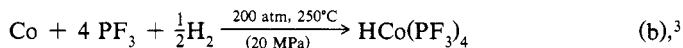
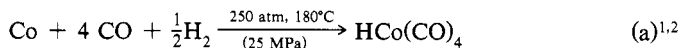
1.10.1. Introduction

Molecular transition-metal hydrides, known since the early 1930s, cover a variety of structural types involving mono- and bidentate hydrogen atoms. Their synthesis is described here. Reactions yielding reversible transition and inner transition-metal hydrides are discussed in §1.12.

(J.J. ZUCKERMAN)

1.10.2. from the Elements.

Few examples exist for preparing molecular transition-metal hydrides from the bulk metal. Hydride complexes of Co and Fe are prepared from the bulk metal, H_2 and CO or a phosphine ligand $[PF_3]$, or $o\text{-C}_6\text{H}_4(\text{PEt}_2)_2$ at high T and P:



Cocondensation of metal-atom vapors and organic ligands yields transition-metal hydrides as well as other organometallics (see Table 1)⁶. The bulk metal is vaporized at a controlled rate by resistance heating, laser heating or electron bombardment under vacuum [$<10^{-3}$ torr (<0.1 Pa)]. The atoms condense either on the cooled walls ($<-100^\circ\text{C}$) of the vacuum chamber with an excess of the organic compound or into a solution of the compound in an inert solvent. Yields of hydride often are based on the amount of metal evaporated.

(T. J. LYNCH)

1. W. Hieber, H. Schulten, B. Marin, *Z. Anorg. Allg. Chem.*, **240**, 261 (1939).
2. M. Orchin, *Acc. Chem. Res.*, **14**, 259 (1981).
3. T. Kruck, K. Baur, W. Lang, *Chem. Ber.*, **101**, 138 (1968).
4. J. Chatt, F. A. Hart, R. G. Hayter, *Nature (London)*, **187**, 55 (1960).
5. J. Chatt, F. A. Hart, D. T. Rosevear, *J. Chem. Soc.*, 5504 (1961).
6. P. L. Timms, T. W. Turney, *Adv. Organomet. Chem.*, **15**, 53 (1977).

TABLE 1. TRANSITION-METAL HYDRIDES SYNTHESIZED BY METAL-ATOM COCONDENSATION WITH ORGANIC LIGANDS

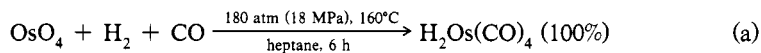
Metal hydride (yield in %)	Organic compound	Ref.
$\text{h}^5\text{-C}_8\text{H}_{11}\text{CrH}(\text{PF}_3)_3$ (2)	1,5-Cyclooctadiene, PF_3	7
$\text{h}^5\text{-C}_5\text{H}_5\text{MoH}_2$ (30–50)	Cyclopentadiene	8,9
$(\text{h}^5\text{-C}_9\text{H}_7)_2\text{MoH}_2$	Indene	9
$\text{h}^5\text{-C}_9\text{H}_8\text{MoH}(\text{C}_5\text{H}_5\text{-h}^5)$	Indene	9
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{WH}_2$ (40–60)	Cyclopentadiene	8,9
$\text{C}_6\text{H}_6\text{WH}(\text{C}_5\text{H}_5\text{-h}^5)$ (30)	Benzene, cyclopentadiene	9
$\text{C}_6\text{H}_5\text{MeWH}(\text{C}_5\text{H}_5\text{-h}^5)$ (55)	Toluene, cyclopentadiene	9
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{WH}_2$	Indene	9
$\text{h}^6\text{-C}_9\text{H}_8\text{WH}(\text{C}_9\text{H}_7\text{-h}^5)$	Indene	9
$\text{H}_2\text{Fe}(\text{PF}_3)_4$	Propene, PF_3	10
$(\text{PMe}_3)_3\text{HFeCH}_2\text{PMe}_2$ (6)	Trimethylphosphine	11
$(1,3\text{-C}_4\text{H}_6)_2\text{CoH}$	1,3-Butadiene, isobutane	12
$(1,3\text{-pentadiene})_2\text{CoH}$	1,4-Pentadiene	12

7. E. A. K. von Gustorf, O. Jaenicke, O. Wolfbeis, C. R. Eady, *Angew. Chem., Int. Ed. Engl.*, **14**, 278 (1975).
8. M. T. D'Annello, E. K. Barefield, *J. Organomet. Chem.*, **76**, C50 (1974).
9. E. M. Van Dam, W. N. Brent, M. P. Silvon, P. S. Skell, *J. Am. Chem. Soc.*, **97**, 465 (1975).
10. C. Francis, B.Sc. Thesis, Univ. Bristol, England (1974); P. W. Taylor, B.Sc. Thesis, Univ. Bristol, England (1974).
11. P. L. Timms, T. W. Turney, unpublished results.
12. P. S. Skell, M. J. McGlinchey, *Angew. Chem., Int. Ed. Engl.*, **14**, 195 (1975).

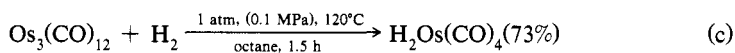
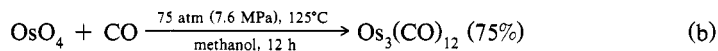
1.10.3. by Hydrogenation

1.10.3.1. of Metal Oxides.

When OsO_4 (Extremely toxic²; all manipulations should be carried out in a well-ventilated hood) is treated with H_2 and CO in a ratio of 1:3 at high T and P, $\text{H}_2\text{Os}(\text{CO})_4$ is formed in high yield¹:



The polynuclear dihydride $\text{H}_2\text{Os}_3(\text{CO})_{10}$ is prepared in two steps from OsO_4 by first preparing² $\text{Os}_3(\text{CO})_{12}$ then treating this with H_2 at 1 atm³.



(T. J. LYNCH)

1. F. L'Eplattenier, F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).
2. B. F. G. Johnson, J. Lewis, *Inorg. Synth.*, **13**, 93 (1972).

174 1.10. Formation of Bonds between Hydrogen and Transition Metals

TABLE 1. TRANSITION-METAL HYDRIDES SYNTHESIZED BY METAL-ATOM COCONDENSATION WITH ORGANIC LIGANDS

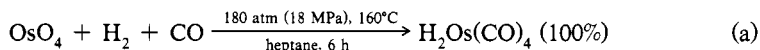
Metal hydride (yield in %)	Organic compound	Ref.
$\text{h}^5\text{-C}_8\text{H}_{11}\text{CrH}(\text{PF}_3)_3$ (2)	1,5-Cyclooctadiene, PF_3	7
$\text{h}^5\text{-C}_5\text{H}_5\text{MoH}_2$ (30–50)	Cyclopentadiene	8,9
$(\text{h}^5\text{-C}_9\text{H}_7)_2\text{MoH}_2$	Indene	9
$\text{h}^5\text{-C}_9\text{H}_8\text{MoH}(\text{C}_9\text{H}_7\text{-h}^5)$	Indene	9
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{WH}_2$ (40–60)	Cyclopentadiene	8,9
$\text{C}_6\text{H}_6\text{WH}(\text{C}_5\text{H}_5\text{-h}^5)$ (30)	Benzene, cyclopentadiene	9
$\text{C}_6\text{H}_5\text{MeWH}(\text{C}_5\text{H}_5\text{-h}^5)$ (55)	Toluene, cyclopentadiene	9
$(\text{h}^5\text{-C}_9\text{H}_7)_2\text{WH}_2$	Indene	9
$\text{h}^6\text{-C}_9\text{H}_8\text{WH}(\text{C}_9\text{H}_7\text{-h}^5)$	Indene	9
$\text{H}_2\text{Fe}(\text{PF}_3)_4$	Propene, PF_3	10
$(\text{PMe}_3)_3\text{HFeCH}_2\text{PMe}_2$ (6)	Trimethylphosphine	11
$(1,3\text{-C}_4\text{H}_6)_2\text{CoH}$	1,3-Butadiene, isobutane	12
$(1,3\text{-pentadiene})_2\text{CoH}$	1,4-Pentadiene	12

7. E. A. K. von Gustorf, O. Jaenicke, O. Wolfbeis, C. R. Eady, *Angew. Chem., Int. Ed. Engl.*, **14**, 278 (1975).
8. M. T. D'Annello, E. K. Barefield, *J. Organomet. Chem.*, **76**, C50 (1974).
9. E. M. Van Dam, W. N. Brent, M. P. Silvon, P. S. Skell, *J. Am. Chem. Soc.*, **97**, 465 (1975).
10. C. Francis, B.Sc. Thesis, Univ. Bristol, England (1974); P. W. Taylor, B.Sc. Thesis, Univ. Bristol, England (1974).
11. P. L. Timms, T. W. Turney, unpublished results.
12. P. S. Skell, M. J. McGlinchey, *Angew. Chem., Int. Ed. Engl.*, **14**, 195 (1975).

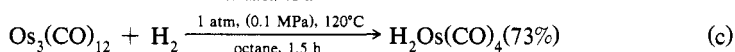
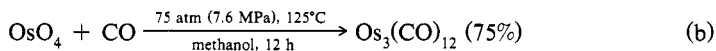
1.10.3. by Hydrogenation

1.10.3.1. of Metal Oxides.

When OsO_4 (Extremely toxic²; all manipulations should be carried out in a well-ventilated hood) is treated with H_2 and CO in a ratio of 1:3 at high T and P, $\text{H}_2\text{Os}(\text{CO})_4$ is formed in high yield¹:



The polynuclear dihydride $\text{H}_2\text{Os}_3(\text{CO})_{10}$ is prepared in two steps from OsO_4 by first preparing² $\text{Os}_3(\text{CO})_{12}$ then treating this with H_2 at 1 atm³.



(T. J. LYNCH)

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2. B. F. G. Johnson, J. Lewis, *Inorg. Synth.*, **13**, 93 (1972).

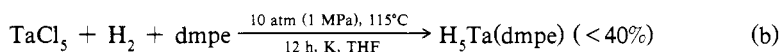
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1.10.3.2. of Metal Salts.

Transition-metal salts are used to synthesize hydrides incorporating the trifluorophosphine ligand¹, PF₃ (Table 1). The reactions are performed at high T and at high P of H₂ and PF₃. Powdered Cu or Zn in the reaction mixture acts as a reducing agent and halogen acceptor. The yields are high:



When transition-metal salts are combined with H₂, alkali-metal and free-ligand polyhydrides result, e.g., for the Ta hydride²:



where dmpe = bis(dimethylphosphino)ethane and THF = tetrahydrofuran. The yields are variable, but when the Ta source is [TaPh₆][−], reproducible yields of 30–40% are obtained. The hydride ligands can be exchanged for deuterium [60 atm, (6 MPa), 80°C], and this complex catalyzes the exchange of hydrogen on benzene.

Binary transition-metal acetates also form hydrides when treated with free ligand, H₂ and Na amalgam. The Mo dimer forms a tetrahydride³:

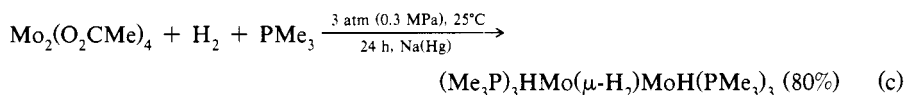


TABLE 1. TRIFLUOROPHOSPHINE-HYDRIDE COMPLEXES
PREPARED FROM TRANSITION-METAL SALTS

Metal salt	Conditions	Product (yield, %)
ReCl ₅	$\xrightarrow[\text{H}_2 (100 \text{ atm, 10 MPa), } 300^\circ\text{C}]{\text{Cu, PF}_3 (250 \text{ atm, 25 MPa),}}$	HRe(PF ₃) ₅ (40)
FeI ₂	$\xrightarrow[\text{H}_2 (100 \text{ atm, 10 MPa), } 250^\circ\text{C}]{\text{Zn, PF}_3 (300 \text{ atm, 30 MPa),}}$	H ₂ Fe(PF ₃) ₄ (trace)
RuCl ₃	$\xrightarrow[\text{H}_2 (100 \text{ atm, 10 MPa), } 270^\circ\text{C}]{\text{Cu, PF}_3 (300 \text{ atm, 30 MPa),}}$	H ₂ Ru(PF ₃) ₄ (70)
OsCl ₃	$\xrightarrow[\text{H}_2 (100 \text{ atm, 10 MPa), } 270^\circ\text{C}]{\text{Cu, PF}_3 (400 \text{ atm, 41 MPa),}}$	H ₂ Os(PF ₃) ₄ (80)
CoI ₂	$\xrightarrow[\text{H}_2 (100 \text{ atm, 10 MPa), } 170^\circ\text{C}]{\text{Cu, PF}_3 (50\text{--}300 \text{ atm, } 5\text{--}30 \text{ MPa),}}$	HCo(PF ₃) ₄ (100)
RhCl ₃	$\xrightarrow[\text{H}_2 (100 \text{ atm, 10 MPa), } 70^\circ\text{C}]{\text{Cu, PF}_3 (90 \text{ atm, } 9 \text{ MPa),}}$	HRh(PF ₃) ₄ (100)
IrCl ₃	$\xrightarrow[\text{H}_2 (45 \text{ atm, } 46 \text{ MPa), } 215^\circ\text{C}]{\text{Cu, PF}_3 (160 \text{ atm, } 16 \text{ MPa),}}$	HIr(PF ₃) ₄ (100)

1.10. Formation of Bonds between Hydrogen and Transition Metals 175

1.10.3. by Hydrogenation

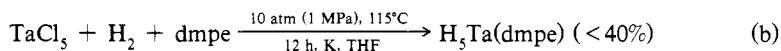
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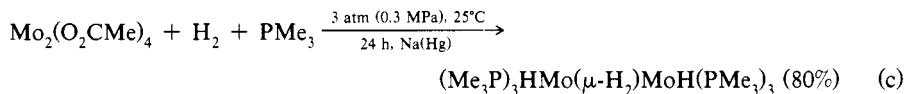


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RuCl ₃	$\xrightarrow[\text{H}_2 \text{ (100 atm, 10 MPa), 270}^\circ\text{C}]{\text{Cu, PF}_3 \text{ (300 atm, 30 MPa),}}$	H ₂ Ru(PF ₃) ₄ (70)
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Niobium pentachloride is used in the synthesis of $\text{NbH}_3(\text{C}_5\text{H}_5\text{-h}^5)_2$; H_2 [800 atm (81 MPa)], $\text{Na}(\text{C}_5\text{H}_5)$, NaBH_4 and NbCl_5 form the trihydride in 20–30% yield. The initial source of the hydride ligand is the NaBH_4 , but these are in fast exchange with H_2 , for separate experiments demonstrate the loss of H_2 at 80°C and also hydride exchange with deuterium of benzene- d_6 . The corresponding Ta, Mo and W hydrides, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$ and $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{MH}_2$, $\text{M} = \text{Mo, W}$, do not require H_2 in their syntheses but only NaBH_4 , reflecting the higher stability of these complexes⁵.

The Nb cluster Nb_6I_{11} absorbs H_2 at atm P above 420°C to form⁶ $\text{HNb}_6\text{I}_{11}$.

Metal salts are used in the preparation of metal-carbonyl hydrides; e.g., $\text{HCo}(\text{CO})_4$ is made⁷ by heating CoS or CoX_2 ($\text{X} = \text{I, Br, Cl}$) with H_2 and CO at 200 atm (20 MPa) and 180°C in the presence of Cu. The Ru cluster, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, is prepared by bubbling CO through RuCl_3 in refluxing EtOH for 4 h, then treating with CO [40 atm (4 MPa)] and H_2 [80 atm (8 MPa)] at 75–100°C for 3 days^{8,9}.

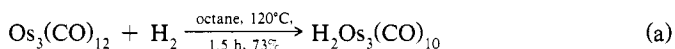
(T. J. LYNCH)

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1.10.3.3. of Metal Carbonyls.

Transition-metal carbonyls are a source of mono- and polynuclear metal-hydride complexes¹. Osmium carbonyls are the most versatile, e.g., $\text{Os}(\text{CO})_5$ and $\text{Os}_3(\text{CO})_{12}$ react with H_2 at 80 atm (8.1 MPa) at 100°C in 6 h to form $\text{H}_2\text{Os}(\text{CO})_4$. Whereas $\text{H}_2\text{Ru}(\text{CO})_4$ can be observed only under high H_2 pressure on $\text{Ru}_3(\text{CO})_{12}$ by IR spectroscopy, phosphine substitution for carbonyls stabilizes hydride products. Therefore, $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ (50%) can be prepared from the hydrogenation for 12 h of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ at 120 atm (12 MPa) and 130°C in tetrahydrofuran (THF)³. Likewise, $\text{H}_3\text{Fe}_3(\mu_3\text{-COMe})(\text{CO})_9$ is unstable relative to H_2 elimination, but $\text{H}_3\text{Fe}_3(\mu_3\text{-COMe})(\text{CO})_7(\text{SbPh}_3)_2$ can be isolated in fair yield by the hydrogenation of $\text{HFe}_3(\mu_3\text{-COMe})(\text{CO})_{10}$ in the presence of SbPh_3 .

The coordinatively unsaturated cluster $\text{Os}_3\text{H}_2(\text{CO})_{10}$ is formed⁵ at atm P:



This method, which does not require high-P apparatus, is also applicable to the synthesis of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ (55%)^{6,7} and $\text{H}_4\text{Re}_4(\text{CO})_{12}$ (55%)⁶ from $\text{Re}_2(\text{CO})_{10}$; $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (88%) from $\text{Ru}_3(\text{CO})_{12}$; $\text{H}_4\text{Os}_4(\text{CO})_{12}$ (29%) from $\text{Os}_3(\text{CO})_{12}$; and $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ (83%)⁵ from $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$.

176 1.10. Formation of Bonds between Hydrogen and Transition Metals
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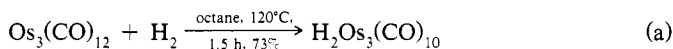
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Hydrogenolysis of metal carbonyls, such as $\text{Mn}_2(\text{CO})_{10}$ [250 atm (25 MPa), 200°C] or $\text{Co}_2(\text{CO})_8$ [250 atm (25 MPa), 110°C], leads to metal-metal bond cleavage, forming $\text{HMn}(\text{CO})_5$ ⁸ or $\text{HCo}(\text{CO})_4$ ⁹. The conversion of $\text{Co}_2(\text{CO})_8$ to $\text{HCo}(\text{CO})_4$ is the rate-determining step in Co-catalyzed hydroformylations at high P and T. Tertiary amines, nitrogen heterocycles, tertiary phosphorus bases or halide ions enhance the rate of $\text{HCo}(\text{CO})_4$ formation¹⁰; e.g., pyridine can increase the rate of $\text{HCo}(\text{CO})_4$ formation 300-fold at 40°C.

Metal dimers containing cyclopentadienyl ligands also can be separated to monomers with H_2 as for $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ at 150 atm (15 MPa) and 70°C to yield¹¹ $\text{HCr}(\text{C}_5\text{H}_5\text{-h}^5)(\text{CO})_3$. Mixed-metal hydride clusters may be synthesized from the H_2 -assisted condensation of two different metal carbonyls. When $\text{Os}_3(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{12}$ reacts with $\text{Ni}_2(\text{C}_5\text{H}_5\text{-h}^5)_2(\text{CO})_2$ in the presence of H_2 at atm P, the mixed-metal clusters $\text{M}_3(\mu\text{-H})_3\text{Ni}(\text{C}_5\text{H}_5\text{-h}^5)(\text{CO})_9$ [$\text{M} = \text{Ru}$ (39%), Os (70%)] are formed¹².

The addition of H_2 to metal carbonyls also occurs with clusters containing noncarbonyl ligands, e.g., $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$ react with H_2 at atm P in refluxing hexane for 2 h to give $\text{H}_3\text{M}_3(\mu_3\text{-COMe})(\text{CO})_9$ [$\text{M} = \text{Ru}$ (93%), Os (79%)]¹³. The hydride ligands bridge the metal-metal bonds. The reaction¹⁴ proceeds by dissociation of a carbonyl ligand prior to the rate-determining oxidative addition of H_2 . Under severe conditions [CO , H_2 , 34 atm (3.4 MPa), 130°C, 23 h, $\text{M} = \text{Ru}$] the methoxycarbonyl ligand is hydrogenated fully to dimethyl ether, while the cluster is isolated as $\text{Ru}_3(\text{CO})_{12}$.

Noncarbonyl ligands can participate more readily in the hydrogenation of the metal carbonyl¹⁵ as for $\text{Ru}_3(\text{CO})_{11}(\text{CNBu-t})$. Bubbling H_2 through the cluster in cyclohexane at reflux for 1 h yields $\text{HRu}_3(\mu_3\text{-HCNBu-t})(\text{CO})_9$ (52%) by addition of H_2 to the coordinated isocyanide. These reactions require milder conditions than those used for the unfunctionalized $\text{Ru}_3(\text{CO})_{12}$ with H_2 .

Triruthenium dodecacarbonyl is functionalized with two edge-bridging bisphosphine or bisarsine ligands to form $\text{Ru}_3(\text{CO})_8(\text{L-L})_2$, where $\text{L-L} = \text{bis}(\text{diphenylphosphino})\text{methane}$ or $\text{bis}(\text{diphenylarsino})\text{methane}$, and then treated with H_2 as with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ above. The imposed retention of the trinuclear Ru frame by the bidentate ligands could favor formation of the Ru analogue of $\text{H}_2\text{Os}_3(\text{CO})_{10}$; however, concomitant with H_2 addition to the cluster is cleavage of the phenyl-phosphine or -arsine bond to yield the metal hydride, $\text{Ru}_3(\mu\text{-H})_2[\mu\text{-P}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})_2]_2(\text{CO})_6$

(T. J. LYNCH)

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2. F. L'Eplattenier, F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).
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4. J. B. Keister, M. W. Payne, M. J. Muscatella, *Organometallics*, **2**, 219 (1983).
5. S. A. R. Knox, J. W. Koepke, M. A. Andrews, H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
6. H. D. Kaesz, S. A. R. Knox, J. W. Koepke, R. B. Saillant, *J. Chem. Soc., Chem. Comm.*, 477 (1971).
7. Another satisfactory route to this compound is described: M. A. Andrews, S. W. Kirtley, H. D. Kaesz, *Inorg. Synth.*, **17**, 66 (1977).
8. W. Hieber, G. Wagner, *Z. Naturforsch., Teil B*, **13**, 339 (1958).
9. M. Orchin, *Acc. Chem. Res.*, **14**, 259 (1981).
10. A. Sisak, F. Ungváry, L. Markó, *Organometallics*, **2**, 1244 (1983). The $\text{Fe}(\text{CO})_5$ -catalyzed hydrogenation of nitrogen heterocycles is similarly enhanced: T. J. Lynch, M. Banah, H. D. Kaesz, C. R. Porter, *J. Org. Chem.*, **49**, 1266 (1984).

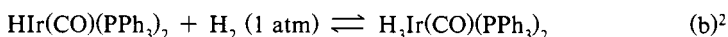
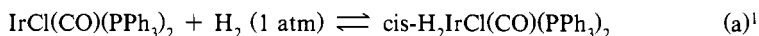
11. E. O. Fischer, W. Hafner, H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).
12. G. Lavigne, F. Papageorgiou, C. Bergounhou, J. J. Bonnet, *Inorg. Chem.*, **22**, 2485 (1983).
13. J. B. Keister, M. W. Payne, M. J. Muscatella, *Organometallics*, **2**, 219 (1983).
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15. M. I. Bruce, R. C. Wallis, *Aust. J. Chem.*, **35**, 709 (1982).

1.10.4. by Oxidative Addition of Hydrogen

1.10.4.1. to Neutral, Coordinatively Unsaturated Species

1.10.4.1.1. Involving Iridium.

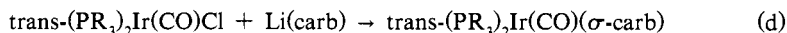
Oxidative addition of H_2 occurs to coordinatively unsaturated complexes of Ir(I):



where dppe = $Ph_2P(CH_2)_2PPh_2$. The kinetics of the addition of H_2 to square-planar Ir(I) complexes are known^{4,5}.

Oxidative addition of H_2 also occurs to the $[Ir(\mu-SBu-t)(CO)(PR_3)_2]_2$ ($R = Me, Ph, NMe_2, OMe$) thiolato-bridged dinuclear Ir complexes. These react irreversibly with H_2 to give quantitative yields of the thiolato-bridged dihydrido-iridium complexes $[Ir(H)(\mu-SBu-t)(CO)(PR_3)_2]_2$. This complex is diamagnetic and contains an Ir—Ir single bond. The dihydrido complex can be protonated. The interaction between H_2 and $[Ir(\mu-SBu-t)(CO)(PR_3)_2]_2$ can be interpreted as a one-electron oxidative addition to each metal atom. An electron-pair coupling interaction between the two Ir^{2+} (d^7) is necessary for each Ir to attain a closed-shell configuration and is in accord with the diamagnetic character of these complexes. In the dihydrido complex, $[Ir(H)(\mu-SBu-t)(CO)P(OMe)_3]_2$, each Ir is in a rectangular-pyramidal environment with an Ir—Ir distance of 267.3 pm. The formation of the dihydrido complex occurs through an $Ir^{3+}-Ir^+$ intermediate in which the two hydride ligands are bound to the same metal atom^{6,7}.

Iridium complexes containing 1,2- and 1,7-dicarba-closo-dodecarborane(12) (carb) are formed^{8,9} through a metal-carbon σ bond:



These complexes are isoelectronic and isostructural with the bis-phosphine Ir carbonyl chloride complex, but they differ in two respects: (a) the reaction with H_2 is irreversible and (b) the oxidative addition of H_2 yields three different cis isomers as a result of a solvent dependence for this addition. The complexes $trans-(PR_2R')_2Ir(CO)(\sigma-carb)$ ($R = C_6H_5$; $R' = C_6H_5, CH_3$) react with H_2 or D_2 , giving the $(PR_2R')_2IrH_2$ (or D_2) $(CO)(\sigma-carb)$ dihydrides or dideuterides. These complexes are colorless crystalline compounds, nonelectrolytes in solution and stable with respect to thermal loss of either carborane or H_2 ; however, they are light sensitive.

178 1.10. Formation of Bonds between Hydrogen and Transition Metals

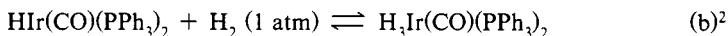
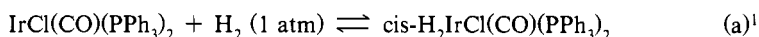
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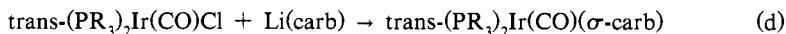
Oxidative addition of H_2 occurs to coordinatively unsaturated complexes of Ir(I):



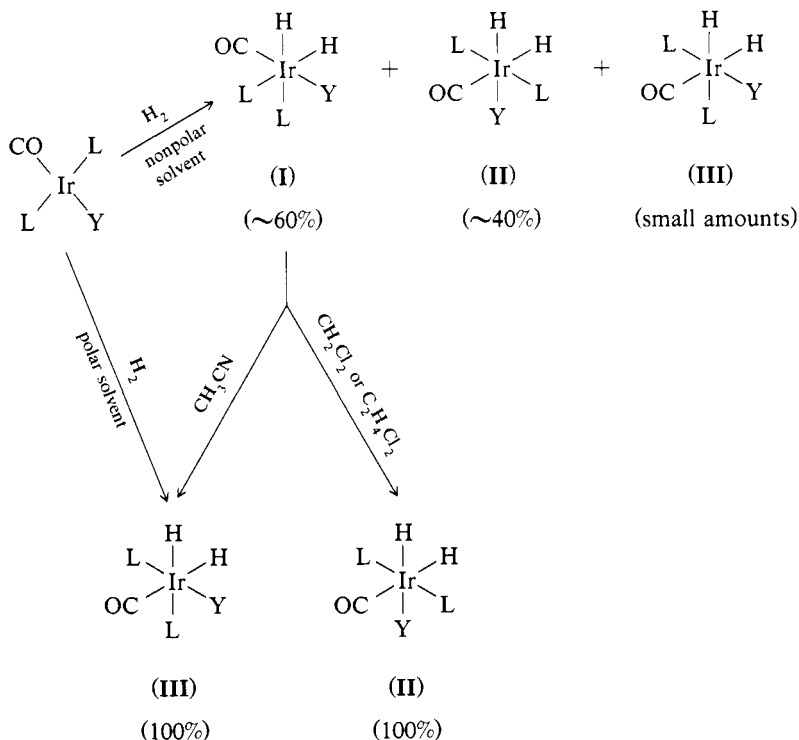
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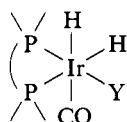


These complexes are isoelectronic and isostructural with the bis-phosphine Ir carbonyl chloride complex, but they differ in two respects: (a) the reaction with H_2 is irreversible and (b) the oxidative addition of H_2 yields three different cis isomers as a result of a solvent dependence for this addition. The complexes $trans-(PR_2R')_2Ir(CO)(\sigma\text{-carb})$ ($R = C_6H_5$; $R' = C_6H_5, CH_3$) react with H_2 or D_2 , giving the $(PR_2R')_2IrH_2$ (or D_2) $(CO)(\sigma\text{-carb})$ dihydrides or dideuterides. These complexes are colorless crystalline compounds, nonelectrolytes in solution and stable with respect to thermal loss of either carborane or H_2 ; however, they are light sensitive.

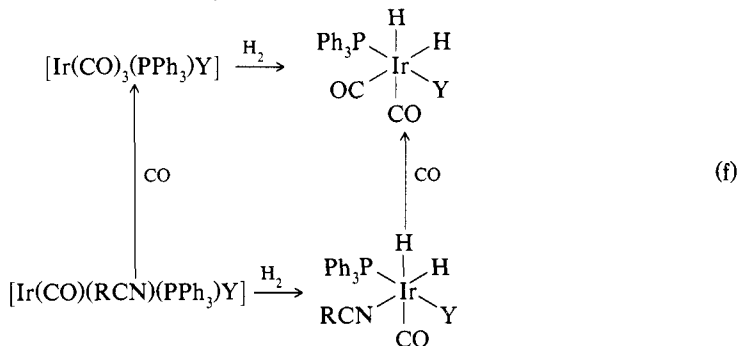


where $\text{L} = \text{PPh}_3, \text{PMePh}_2$; $\text{Y} = [2\text{-H-1,2-B}_{10}\text{C}_2\text{H}_{10}]^-$, $[7\text{-R-1,7-B}_{10}\text{C}_2\text{H}_{10}]^-$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$). Solid $1\text{-}[(\text{PPh}_3)_2\text{Ir}(\text{CO})](2\text{-CH}_3\text{-1,2-B}_{10}\text{C}_2\text{H}_{10})$ is insoluble but reacts with H_2 . The reaction is complete in a few seconds at RT under 1 atm of H_2 , yielding a single dihydridocarbonyl iridium(III) isomer (configuration III) that is soluble and stable in organic solvents. Steric effects, resulting from the presence of the large carbonyl and phosphine ligands, determine the stereochemistry of the oxidative addition reactions of the carbonyl-iridium(I) complexes.

$\text{Trans-}[\text{Ir}(\text{CO})(\text{PPh}_3)_2(7\text{-C}_6\text{H}_5\text{-1,7-B}_{10}\text{C}_2\text{H}_{10})]$ reacts with RCN ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) at RT to give monophosphino nitrile Ir(I) complexes, $[\text{Ir}(\text{CO})(\text{RCN})(\text{PPh}_3)\text{Y}]$ ($\text{Y} = 7\text{-C}_6\text{H}_5\text{-1,7-B}_{10}\text{C}_2\text{H}_{10}$). When $[\text{Ir}(\text{CO})(\text{RCN})(\text{PPh}_3)\text{Y}]$ is treated with the bidentate ligand dppe, facile and irreversible displacement of both RCN and PPh_3 ligands occurs to give the four-coordinated complex $[\text{Ir}(\text{CO})(\text{dppe})\text{Y}]$. This complex reacts with H_2 in a benzene suspension to give the white dihydro complex⁹:

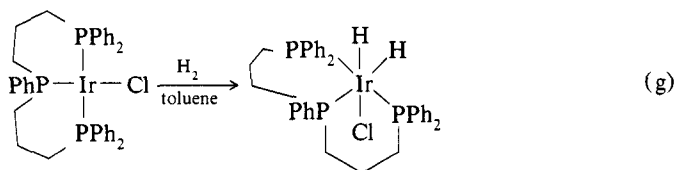


The reactions of $[\text{Ir}(\text{CO})(\text{RCN})(\text{PPh}_3)_2\text{Y}]$ are:



The ^1H NMR spectrum for $[\text{H}_2\text{Ir}(\text{CO})(\text{RCN})(\text{PPh}_3)(7\text{-C}_6\text{H}_5\text{-1,7-B}_{10}\text{C}_2\text{H}_{10})]$ shows two doublets that have chemical shift and coupling constant values consistent with a structure in which the two mutually cis-hydride ligands are trans to CO and RCN, respectively.

Bis(3-diphenylphosphinopropyl)phenylphosphinechloroiridium(I) is prepared from $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ and the triphosphine ligand. This complex reacts with H_2 in toluene¹⁰:



IR and NMR spectroscopy indicate that the dihydrido complex is a cis-mer O_h .

Section 1.10.4 presents enthalpy data for the oxidative addition of substrates to $\text{Ir}(\text{I})$ complexes. Table 1 summarizes thermochemical data¹¹ for the oxidative addition of H_2 to $\text{Ir}(\text{I})$ complexes.

(J. TOPICH)

1. L. Vaska, R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).
2. L. Malatesta, G. Caglio, M. Angoletta, *J. Chem. Soc.*, 6974 (1965).
3. B. J. Fisher, R. Eisenberg, *Organometallics*, **2**, 764 (1983).
4. P. B. Chock, J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).
5. J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970).
6. A. Thorez, A. Maisonnat, R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, 518 (1977).
7. J. J. Bonnet, A. Thorez, A. Maisonnat, J. Galy, R. Poilblanc, *J. Am. Chem. Soc.*, **101**, 5940 (1979).
8. B. Longato, F. Morandini, S. Bresadola, *Inorg. Chem.*, **15**, 650 (1976).
9. B. Longato, S. Bresadola, *Inorg. Chim. Acta*, **33**, 189 (1979).
10. E. Arpac, L. Dahlenburg, *Z. Naturforsch., Teil B*, **36**, 672 (1981).
11. J. U. Mondal, D. M. Blake, *Coord. Chem. Rev.*, **47**, 205 (1982).
12. L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).
13. W. Strohmeier, *J. Organomet. Chem.*, **32**, 137 (1971).
14. W. Strohmeier, F. J. Muller, *Z. Naturforsch., Teil B*, **24**, 931 (1969).
15. L. Vaska, M. F. Werneke, *Trans. N.Y. Acad. Sci.*, **70** (1971).

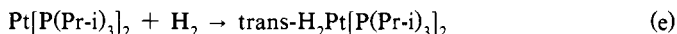
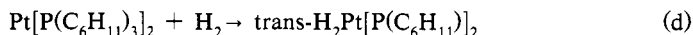
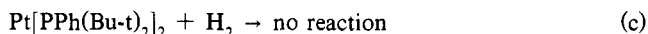
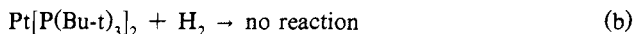
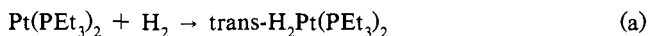
TABLE 1. THERMOCHEMICAL DATA FOR THE REACTION OF TRANS-[IRXL'L₂] WITH H₂

L	X	L'	—ΔH (kJ mol ⁻¹)	T (°C)	Solvent	Ref.
PPh ₃	Cl	CO	62.3	30	Chlorobenzene	12
			66.1	80	Toluene	14
	Br		71.1	30	Chlorobenzene	15
			34.7	80		14
	I		79.5	30		12
			11.3	80	Toluene	12
P(Tol-4) ₃	Cl	55.2			14	
P(C ₆ H ₁₁) ₃		50.2	30		15	
		44.8	80	Toluene	13, 14	
		51.9			13, 14	
P(OPh) ₃	I	75.3			13, 14	
	Cl	51.5			13, 14	
	Br	40.6			13, 14	
	I	11.3			13, 14	
P(Pr-i) ₃	Cl	44.4			13, 14	
	Br	54.8			13, 14	
	I	17.2			13, 14	
PEt ₃	Cl	55.6		Chlorobenzene	15	
P(Bu-t)Ph ₂		48.1		Toluene	13, 14	
P(CH ₂ Ph) ₃		62.3			13, 14	

1.10.4.1.2. Involving Platinum.

Two-coordinated 14-electron complexes of Pt, Pt(PR₃)₂, are sources of Pt(0). Preparation of Pt[P(C₆H₁₁)₃]₂ and Pt[PMe(Bu-t)₂]₂ proceeds from Pt(COD)₂ (COD = 1,5-cyclooctadiene) with 2 equivs of the tertiary phosphine¹. Both complexes are air sensitive and dissolve in organic solvents; however, Pt[PMe(Bu-t)₂]₂ decomposes after a few days when stored as a solid under N₂. Bis(tricyclohexylphosphine)Pt in toluene reacts rapidly with H₂ at RT to give white crystals^{2,3} of trans-H₂[P(C₆H₁₁)₃]₂Pt.

Phosphine complexes^{4,5} of Pt(0) and Pd(0) react with small molecules. Not all PdL₂ complexes [where L = PEt₃, P(Bu-t)₃, PPh(Bu-t)₂, P(C₆H₁₁)₃ and P(Pr-i)₃] react with H₂. Strongly electron donating phosphines are necessary for PtL₂ to react with H₂ under normal pressure at RT in benzene:



The reactivity of the Pt phosphine complexes toward H₂ increases in the order P(Bu-t)₃ < < PPh(Bu-t)₂ < P(C₆H₁₁)₃ < P(Pr-i)₃. The cone angles of the phosphines⁶ increase in the order P(Pr-i)₃ (160 ± 10°) < P(C₆H₁₁)₃ (179 ± 10°) ≤ PPh(Bu-t)₂ (170 ± 2°) < P(Bu-t)₃ (182 ± 2°), suggesting that the reactivity of the two-coordinated Pt(0)

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1.10.4. by Oxidative Addition of Hydrogen

1.10.4.1. to Neutral, Coordinatively Unsaturated Species

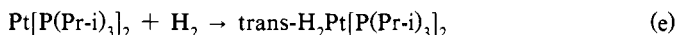
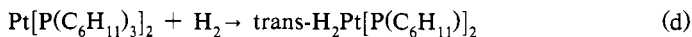
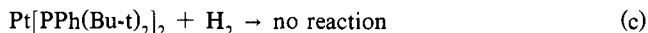
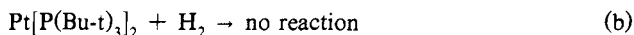
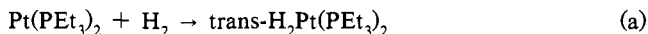
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			51.9			13, 14
	I		75.3			13, 14
P(OPh) ₃	Cl		51.5			13, 14
	Br		40.6			13, 14
	I		11.3			13, 14
P(Pr-i) ₃	Cl		44.4			13, 14
	Br		54.8			13, 14
	I		17.2			13, 14
PEt ₃	Cl		55.6		Chlorobenzene	15
P(Bu-t)Ph ₂			48.1		Toluene	13, 14
P(CH ₂ Ph) ₃			62.3			13, 14

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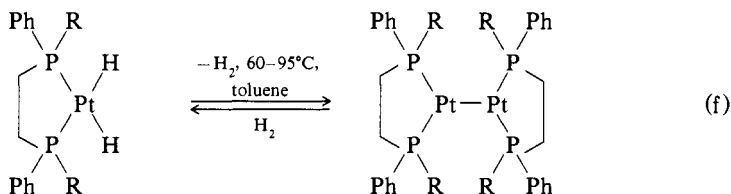


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complexes is governed by the size of the tertiary phosphine. Electronic properties also may be important. The basicity of the phosphines⁷ increases in the order $\text{PPh}(\text{Bu}-t)_2 < \text{P}(\text{Pr}-i)_3 < \text{P}(\text{C}_6\text{H}_{11})_3 < \text{P}(\text{Bu}-t)_3$.

cis-Dihydride diphosphine complexes of Pt^{2+} can be prepared⁸. Four-coordinated, planar d^8 -metal complexes with cis-hydrido ligands are rare, but stable trans-dihydride complexes are isolated with bulky tertiary phosphines^{4,5}, e.g., $[\text{Pt}(\text{Bu}-t)_2\text{P}(\text{CH}_2)_3\text{P}(\text{Bu}-t)_2]_2$ is prepared from $\text{PtCl}_2[(\text{t-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(\text{Bu}-t)_2]$ and Na/Hg (1%) in tetrahydrofuran (THF) at RT. Cis- $\text{H}_2\text{Pt}[(\text{t-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(\text{Bu}-t)_2]$ is prepared from $[\text{Pt}(\text{t-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(\text{Bu}-t)_2]_2$ in toluene by bubbling H_2 through it for 30 min. The cis-dihydride also can be prepared by reducing $\text{PtCl}_2[(\text{t-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(\text{Bu}-t)_2]$ with Na/Hg under H_2 . The reaction of this dimer with D_2 or CHCl_3 is accompanied by formation of a Pt—H-containing species, indicating hydrogen abstraction upon Pt—Pt bond cleavage. Although direct evidence for dissociation to a mononuclear species, $[\text{Pt}[(\text{t-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(\text{Bu}-t)_2]]$, is lacking, the instability in solution suggests Pt—Pt bond cleavage. The mass spectrum⁵ shows the mononuclear ion (m/e 527) along with the parent ion (m/e 1054).

Cis- $\text{H}_2\text{Pt}[\text{Men}(\text{Ph})\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})\text{Men}]$ (Men = 1-menthyl) and cis- $\text{H}_2\text{Pt}[(\text{t-Bu})(\text{Ph})\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{Bu}-t)]$ are prepared⁸ from the corresponding PtCl_2 (diphos) complex by reduction with Na/Hg (1%) in THF under H_2 . These two complexes are stable crystalline solids, and the dihydrogen coordination is reversible in solution.



where $\text{R} = \text{t-Bu}$ or Men. This reaction can be followed by ^1H NMR spectroscopy, and the dimeric nature of the product inferred. The large $|^1J(^{195}\text{Pt}-^1\text{H})|$ and high $\nu(\text{Pt}-\text{H})$ IR frequencies of cis-dihydrides compared with⁹ trans- PtH_2L_2 suggest stronger Pt—H bonding, consistent with the stronger trans influence of the hydride compared with that of the phosphine.

The stability of a cis-dihydride depends on the nature of the diphosphine and increases: $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2 < \text{Men}(\text{Ph})\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})\text{Men} < (\text{t-Bu})(\text{Ph})\text{P}(\text{CH}_2)_2\text{P}(\text{Ph})(\text{Bu}-t) < \text{Men}_2\text{P}(\text{CH}_2)_2\text{PMen}_2 \approx (\text{t-Bu})_2\text{P}(\text{CH}_2)_n\text{P}(\text{Bu}-t)_2$ ($n = 2, 3$).

(J. TOPICH)

1. J. Fornies, M. Green, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1006 (1977).
2. B. L. Shaw, M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 918 (1974).
3. A. Immirzi, A. Musco, G. Carturan, U. Belluco, *Inorg. Chim. Acta*, 12, L23 (1975).
4. T. Yoshida, S. Otsuka, *J. Am. Chem. Soc.*, 99, 2134 (1977).
5. S. Otsuka, *J. Organomet. Chem.*, 200, 191 (1980).
6. C. A. Tolman, *J. Am. Chem. Soc.*, 92, 2956 (1970).
7. C. A. Tolman, *J. Am. Chem. Soc.*, 92, 2953 (1970).
8. T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, S. Otsuka, *J. Am. Chem. Soc.*, 100, 2063 (1978).
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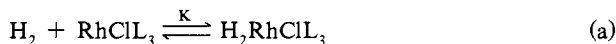
1.10. Formation of Bonds between Hydrogen and Transition Metals 183

1.10.4. by Oxidative Addition of Hydrogen

1.10.4.1. to Neutral, Coordinatively Unsaturated Species

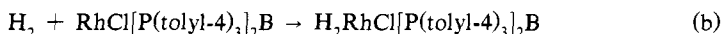
1.10.4.1.3. Involving Rhodium.

The equilibrium constant¹ in toluene at 25°C:

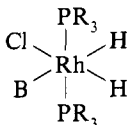


is 18 atm⁻¹ for L = PPh₃, and 40 atm⁻¹ for L = [P(tolyl-4)₃]. The equilibrium for oxidative addition of H₂ is favored for the complex with the better electron-donating phosphine. The equilibrium constant for the sluggish reaction of {RhCl[P(tolyl-4)₃]₂}₂ in toluene at 25°C is 11 atm⁻¹. The equilibrium constant for the p-tolylphosphine dimer is 3.6 times less than that of the analogous monomer, reflecting a reduced electron density at Rh in the Cl-bridged dimer. The absence of a dimer tetrahydride, even under forcing conditions, indicates that the electron-withdrawing nature of the hydride can be transmitted through the chlorine bridge to the other end of the dimer.

The reaction²:



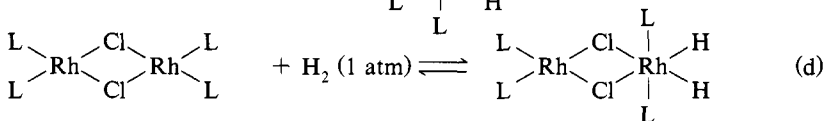
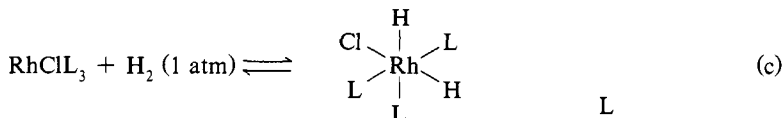
[where B = P(tolyl-4)₃, pyridine (py), tetrahydrothiophene (THTP) and N-methylimidazole (MeIm)] gives dihydride complexes containing trans phosphines and nonequivalent cis hydrides:



For H₂ oxidative addition with RhCl[P(tolyl-4)₃]₂, K (30.1°C) = 29.9 atm⁻¹ and ΔH = -46.0 kJ mol⁻¹, and with RhCl(THTP)[P(tolyl-4)₃]₂, K (30.0°C) = 21.5 atm⁻¹ and ΔH = -48.5 kJ mol⁻¹. Metal-hydrogen bond dissociation energies of 241.0 and 242.3 kJ mol⁻¹ result for the P(tolyl-4)₃ and THTP adducts, respectively, of RhH₂ClB-[P(tolyl-4)₃]₂. Hence the average metal-hydrogen bond energy is insensitive to differences in these two ligands.

Bubbling H₂ through solutions of HRh[P(Pr-i)₃]₂ and HRh[P(Bu-t)₃]₂ yields H₃Rh[P(Pr-i)₃]₂ and H₃Rh[P(Bu-t)₃]₂, respectively³.

Soluble (chlorosilyl)phosphine complexes of Rh(I) can be polymerized into poly(siloxyphosphine) Rh(I) species⁴. In addition, soluble siloxyphosphine-Rh(I) complexes, L₃RhCl and L₄Rh₂Cl₂, where L = [(CH₃)₃SiO]₂(CH₃)Si(CH₂)₂PPh₂, serve as models for their polymeric counterparts.



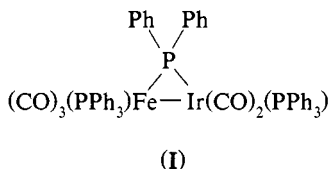
The uptake of H₂ by RhClL₃ is reversible at 25°C, as is the uptake by L₄Rh₂Cl₂. The two siloxyphosphine complexes catalyze the hydrogenation of styrene. The hydrogenation rate is higher for the tris(phosphine) than for the tetrakis(phosphine) complex.

(J. TOPICH)

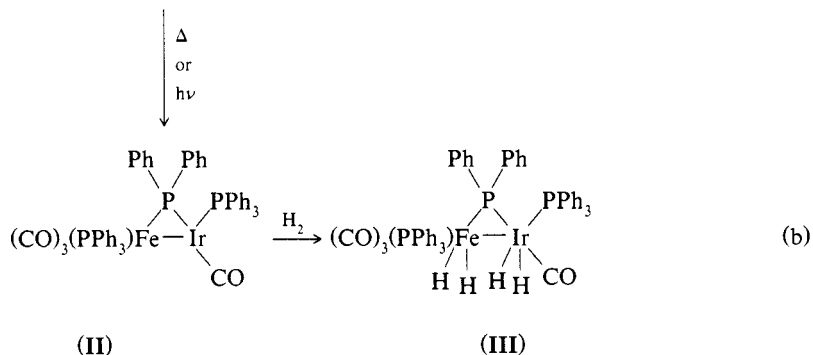
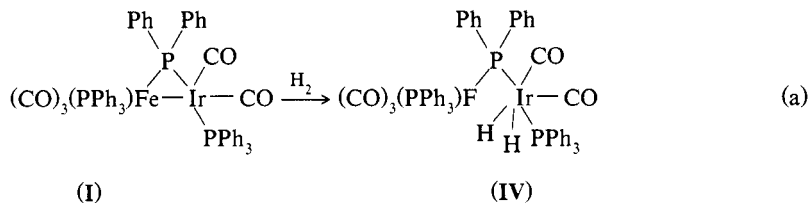
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1.10.4.1.4. Involving Fe—Ir and Ta=Ta Clusters.

Heterobimetallic complexes, $\text{FeIr}(\mu\text{-PPh}_2)(\text{CO})_x(\text{PPh}_3)_2$ ($x = 4-6$), are synthesized¹ from $\text{Li}[\text{Fe}(\text{CO})_4(\text{PPh}_2)]$ with $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$. In the parent complex (I):



both metal centers are saturated coordinatively with 18 valence electrons (with Fe as a two-electron donor), although cleavage of the Fe—Ir bond leads to a vacant coordination site on Ir. Addition of H_2 (1 atm, 25°C) proceeds rapidly and quantitatively to cleave the Fe—Ir bond. Addition of H_2 to the Ir center is indicated by the nuclear magnetic resonance (NMR) of PPh_3 on Ir, which is a doublet of triplets at $\delta = 1.9$ ppm:



Complex (I) also loses CO when heated at 110°C or irradiated ($\lambda = 366$ nm) under N_2 . This product (II) also adds H_2 and a tetrahydride complex (III) is formed. The ^1H NMR spectrum (-40°C) shows four distinct hydride resonances (1 : 1 : 1 : 1). Selective decoupling NMR experiments show that each of the terminal PPh_3 ligand couples to two inequivalent hydrides, suggesting structure (III).

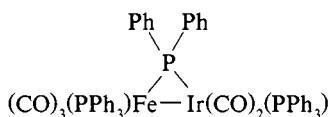
The Ta^{3+} dimer, $\text{Ta}_2\text{Cl}_6(\text{PMe}_3)_4$, reacts readily and irreversibly with H_2 under mild conditions (25°C, 1 atm) to form the Ta^{4+} dimer², $\text{Ta}_2\text{Cl}_6(\text{PMe}_3)_4\text{H}_2$, an example of H_2 addition to a metal-metal multiple bond:

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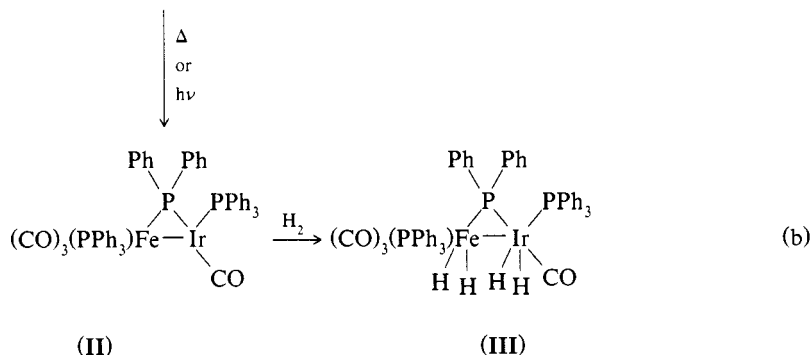
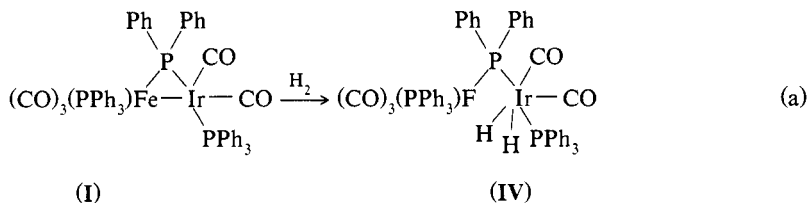
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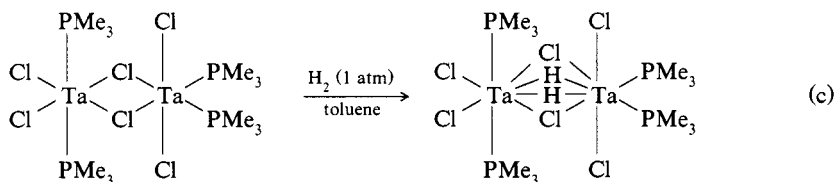
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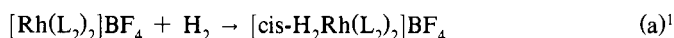
(J. TOPICH)

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1.10.4.2. to Cationic, Coordinatively Unsaturated Species of Rhodium, Ruthenium and Iridium.

Cationic transition-metal complexes activate small molecules and serve as homogeneous catalysts, especially for selective hydrogenation of unsaturated organics. Section 1.10.4.2 deals with coordinatively unsaturated complexes in which the ligands remain coordinated after the oxidative addition of H_2 . In §1.10.4.4 the complexes may or may not be coordinatively unsaturated; complexes that are not must lose ligand(s) before oxidative addition of H_2 . Coordinatively unsaturated complexes are described that exchange ligands either before or after the oxidative addition of H_2 .

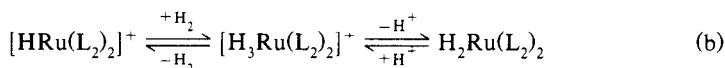
Bis(ditertiaryphosphine)Rh(I) complexes add H_2 reversibly¹:



where L_2 is either 1,3-bis(diphenylphosphino)propane (dppp) or 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)-diop]. The $[\text{H}_2\text{Rh}(\text{diop})_2]^+$ cation is known as the $[\text{ClO}_4]^-$ and $[\text{PF}_6]^-$ salts². When L_2 is bis(diphenylphosphino)methane (dppm) or bis(diphenylphosphino)ethane (dppe), the Rh complex cations are unreactive toward H_2 , whereas a mixture of hydrides is formed when L_2 is bis(diphenylphosphino)butane (dppb).

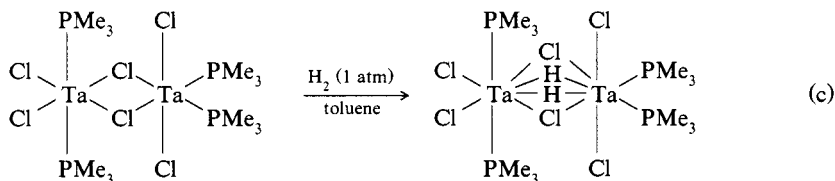
The cations $[\text{cis-H}_2\text{Rh}(\text{dppp})_2]^+$ and $[\text{cis-H}_2\text{Rh}(+)\text{-diop}]_2^+$ are similar to the known³ $[\text{cis-H}_2\text{Rh}[\text{P}(\text{CH}_3)_3]_4]^+$ and show a $\nu(\text{Rh-H})$ stretch in the IR, a pair of multiplets in the high-field nuclear magnetic resonance (NMR) at 25°C and two resonances in the ³¹P NMR. The lower field resonance for each system is attributed to the mutually trans-P atoms, and that at higher field to the P atoms trans to the hydrides. The presence of two ³¹P resonances at all temperatures rules out a cis-trans rearrangement. Both $[\text{cis-H}_2\text{Rh}(\text{dppp})_2]^+$ and $[\text{cis-H}_2\text{Rh}(+)\text{-diop}]_2^+$ lose H_2 on dissolving in solution under Ar.

With similar bidentate phosphines, as well as PMePh_2 , Ru^{2+} hydrides react⁴ with H_2 at RT and ambient P:



1.10. Formation of Bonds between Hydrogen and Transition Metals 185

1.10.4. by Oxidative Addition of Hydrogen



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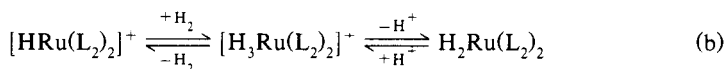
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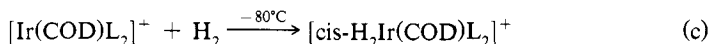
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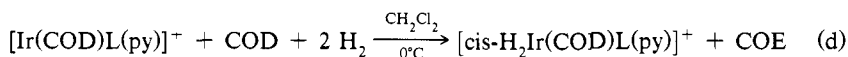
where $L_2 = (\text{PMePh}_2)_2$, dppp, dppb.

The salts $[\text{H}_3\text{Ru}(L_2)]^+$ lose 1 equiv of H_2 on warming in alcohol under Ar. When $L_2 = \text{dppp}$ prolonged heating is required for H_2 loss.

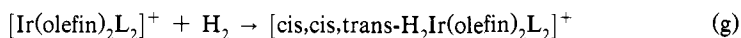
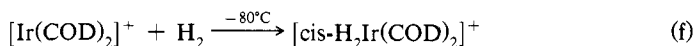
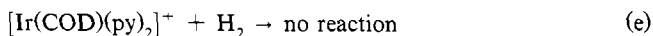
Cationic coordinatively unsaturated Ir^+ complexes react with H_2 in homogeneous hydrogenation reactions.⁵⁻⁷



where $L = 1/2 \text{ diop}$, $1/2 \text{ dppm}$, $\text{P}(\text{Bu-n})_3$, PPh_3 , PMePh_2 ; $\text{COD} = 1,5\text{-cyclooctadiene}$;



where $L = \text{P}(\text{Pr-i})_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$; $\text{COE} = \text{cyclooctene}$;



where olefin = C_2H_4 , $\text{PhCH}=\text{CH}_2$, COE ; $L = \text{PMePh}_2$.

Reaction (c) is reversible. On warming, H_2 is lost and the parent complex is recovered in high yield. If H_2 is bubbled through the solution [Eq. (c)] as it is warmed to RT, the Ir complex is completely hydrogenated to give a polynuclear Ir hydride, $[\text{HL}_2\text{IrH}_3\text{IrHL}_2]^+$. Reaction (d) involves $[\text{Ir}(\text{COD})\text{L}(\text{py})]^+$, the most active hydrogenation catalyst among the Ir complexes in reactions (c)–(g). Reaction (f) shows that electron-withdrawing ligands, such as olefins, do not deactivate the metal toward addition of H_2 . In fact, ^{13}C -NMR evidence^{7,8} supports the reductive character of the addition. An upfield shift in the vinyl-carbon resonances of $[\text{Ir}(\text{COD})_2]^+$ on addition of H_2 suggests that the electron density at the Ir increases.

Electron-donating ligands normally enhance the oxidative addition of H_2 to a metal center, but addition of H_2 to Ir complexes can be promoted by electron-withdrawing ligands and inhibited by electron-donating ones. The addition of H_2 to these complexes may be not oxidative, but reductive in character. This unusual reactivity pattern allows the catalytic hydrogenation systems derived from them to be less susceptible to oxidizing poisons.

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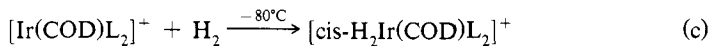
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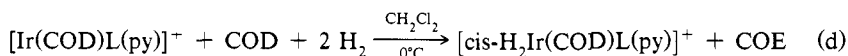
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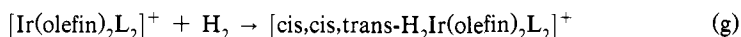
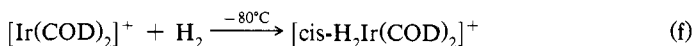
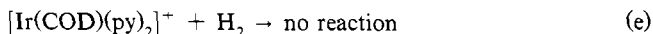
Cationic coordinatively unsaturated Ir^+ complexes react with H_2 in homogeneous hydrogenation reactions.⁵⁻⁷



where $\text{L} = 1/2 \text{ diop}, 1/2 \text{ dppm}, \text{P}(\text{Bu-n})_3, \text{PPh}_3, \text{PMePh}_2$; $\text{COD} = 1,5\text{-cyclooctadiene}$;



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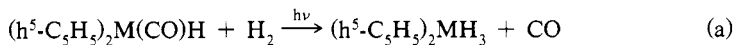
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(J. TOPICH)

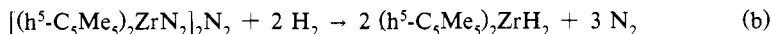
1.10.4.3.1. Involving Niobium, Tantalum and Zirconium.

In the presence of H_2 , $(\eta^5-C_5H_5)_2M(CO)H$ ($M = Nb$ and Ta) can be photolyzed¹:



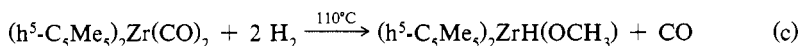
Only 50% of the $(\eta^5-C_5H_5)_2Nb(CO)H$ is converted to the trihydride, whereas $(\eta^5-C_5H_5)_2Ta(CO)H$ converts completely. The reverse of reaction (a) occurs if the photolysis of $(\eta^5-C_5H_5)_2NbH_3$ and $(\eta^5-C_5H_5)_2TaH_3$ is carried out in the presence of CO. Both $(\eta^5-C_5H_5)_2NbH_3$ and $(\eta^5-C_5H_5)_2TaH_3$ lose H_2 when photolyzed in benzene. The 16-electron species $(\eta^5-C_5H_5)_2NbH$ and $(\eta^5-C_5H_5)_2TaH$ are capable of activating carbon-hydrogen bonds in benzene and catalyzing the H-D exchange between D_2 and benzene.

Stirring $[(\eta^5-C_5Me_5)_2ZrN_2]_2N_2$ in toluene with 1 atm of H_2 yields $(\eta^5-C_5Me_5)_2ZrH_2$ quantitatively^{2,3}:

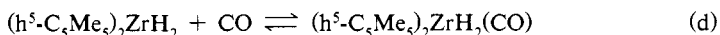


The product is soluble in hydrocarbons and ethers as a monomer, in contrast to the polymeric $[(\eta^5-C_5H_5)_2ZrH_2]_x$. In toluene at $-80^\circ C$ the $(\eta^5-C_5Me_5)_2ZrH_2$ hydrogens exchange with D_2 . At higher T (ca. $50^\circ C$), all 30 methyl hydrogens of the two $\eta^5-C_5Me_5$ rings also exchange with D_2 .

The evolution of 1 equiv of free CO in Eq. (c) suggests that $(\eta^5-C_5Me_5)_2Zr(CO)$ is an intermediate^{3,4}:



Oxidative addition of H_2 to $(\eta^5-C_5Me_5)_2Zr(CO)$ to generate the dihydride is plausible in light of:

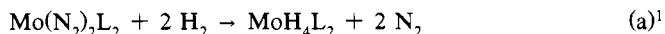


(J. TOPICH)

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3. P. T. Wolczanski, J. E. Bercaw, *Acc. Chem. Res.*, **13**, 121 (1980).
4. J. Manriquez, D. R. McAlister, R. D. Sanner, J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 6733 (1976).

1.10.4.3.2. Involving Molybdenum and Rhenium.

Reaction of $Mo(N_2)_2L_2$, where L is a bidentate tertiary phosphine ligand, occurs with H_2 :



where $L = Ph_2PCH_2CH_2PPh_2(dppe)$, $(3-tolyl)_2PCH_2CH_2P(tolyl-3)_2(dmtpe)$, $(4-tolyl)_2PCH_2CH_2P(tolyl-4)_2(dptpe)$ yields a tetrahydride, and not a dihydride as previously claimed². Reaction (a) can be reversed, although not quantitatively, if N_2 is bubbled through MoH_4L_2 in cyclohexane. Irradiation of $MoH_4(dppe)_2$ under N_2 , however, re-

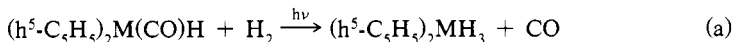
- 1.10. Formation of Bonds between Hydrogen and Transition Metals 187
 1.10.4. by Oxidative Addition of Hydrogen
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tral transition-metal complexes that lose ligand(s) during the reaction. The loss of a coordinated ligand can be photoinduced.

(J. TOPICH)

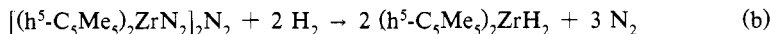
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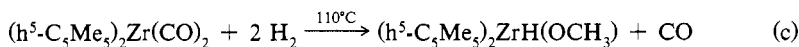
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Stirring $[(\eta^5-C_5Me_5)_2ZrN_2]_2N_2$ in toluene with 1 atm of H_2 yields $(\eta^5-C_5Me_5)_2ZrH_2$ quantitatively^{2,3}:

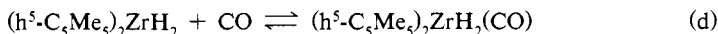


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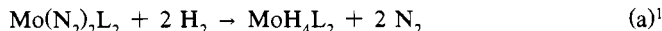


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1.10.4.3.2. Involving Molybdenum and Rhenium.

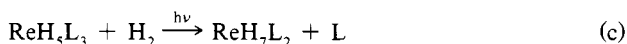
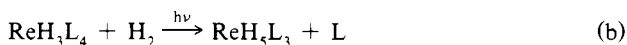
Reaction of $Mo(N_2)_2L_2$, where L is a bidentate tertiary phosphine ligand, occurs with H_2 :



where $L = Ph_2PCH_2CH_2PPh_2(dppe)$, $(3-tolyl)_2PCH_2CH_2P(tolyl)_2(dmtpe)$, $(4-tolyl)_2PCH_2CH_2P(tolyl)_2(dtppe)$ yields a tetrahydride, and not a dihydride as previously claimed². Reaction (a) can be reversed, although not quantitatively, if N_2 is bubbled through MoH_4L_2 in cyclohexane. Irradiation of $MoH_4(dppe)_2$ under N_2 , however, re-

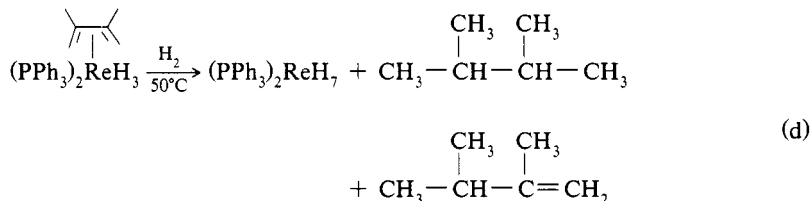
sults in $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ quantitatively^{3,4}. Variable-T ^1H nuclear magnetic resonance (NMR) shows that $\text{MoH}_4(\text{dmtpe})_2$ is stereochemically nonrigid and undergoes an intramolecular exchange in which all the hydride ligands are coupled equally to all ^{31}P nuclei¹.

Photolysis of polyhydride Re complexes under H_2 produces^{4,6}:



where $\text{L} = \text{PMe}_2\text{Ph}$, PMePh_2 , PPh_3 . The ReH_7L_2 product converts thermally and photochemically to the dimer⁶, $\text{Re}_2\text{H}_8\text{L}_4$. In the absence of H_2 , ReH_5L_3 loses the phosphine ligand, L , rather than H_2 , on photolysis^{4,5,7}.

Hydrogenation⁸ of $\text{ReH}_3(\text{PPh}_3)_2(\text{h}^4\text{-2,3-dimethylbutadiene})$ leads to $\text{ReH}_7(\text{PPh}_3)_2$, which is thermally unstable. 2,3-Dimethylbutane and 2,3-dimethylbut-1-ene also are observed as products:



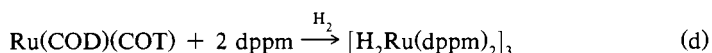
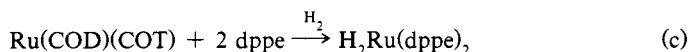
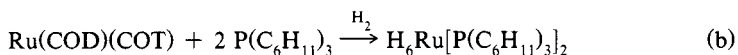
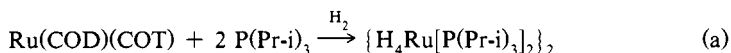
Photolysis⁹ of $(\text{h}^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in the presence of H_2 yields $(\text{h}^5\text{-C}_5\text{H}_5)\text{ReH}_2(\text{CO})_2$.

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5. D. A. Roberts, G. L. Geoffroy, *J. Organomet. Chem.*, **214**, 221 (1981).
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1.10.4.3.3. Involving Ruthenium and Mixed Metal–Ruthenium Clusters.

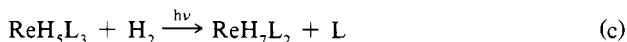
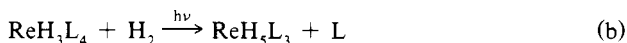
The Ru complex $\text{Ru}(\text{COD})(\text{COT})$ ($\text{COD} = 1,5\text{-cyclooctadiene}$; $\text{COT} = 1,3,5\text{-cyclooctatriene}$) is a precursor to Ru–hydride phosphine complexes¹:



188 1.10. Formation of Bonds between Hydrogen and Transition Metals
 1.10.4. by Oxidative Addition of Hydrogen
 1.10.4.3. to Neutral Species

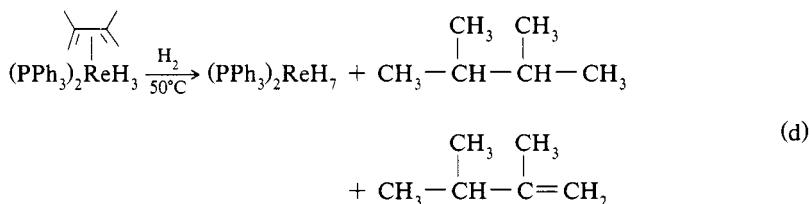
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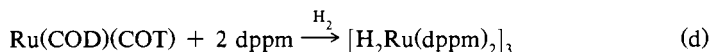
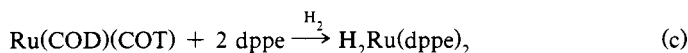
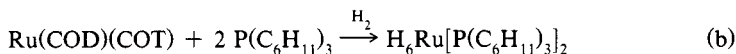
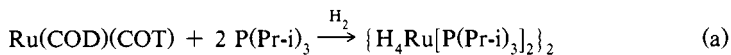
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1.10.4.3.3. Involving Ruthenium and Mixed Metal-Ruthenium Clusters.

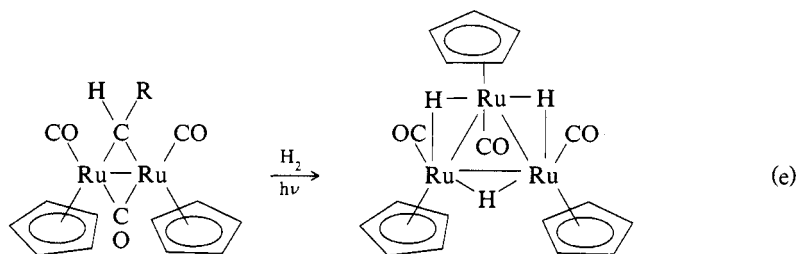
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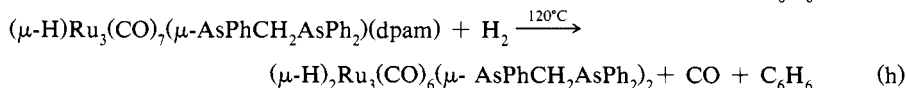
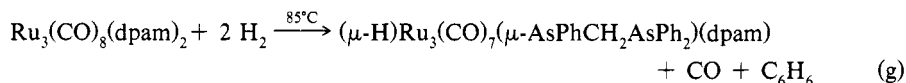
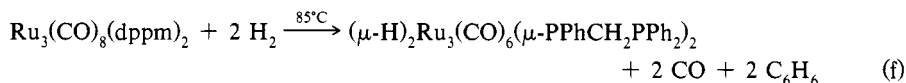
where dppe = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$; dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$.

The Ru-carbonyl clusters react with H_2 ; e.g., $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ is prepared² by bubbling H_2 through $\text{Ru}_3(\text{CO})_{12}$ in n-octane at reflux for 1 h. Likewise, $\text{D}_4\text{Ru}_4(\text{CO})_{12}$ is prepared² using D_2 gas, and $\text{H}_2\text{D}_2\text{Ru}_4(\text{CO})_{12}$ results from $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ and D_2 in refluxing hexane. In contrast to the analogous Os system, no hydrogen exchange with the hydrocarbon solvent occurs with $\text{H}_2\text{D}_2\text{Ru}_4(\text{CO})_{12}$. Reaction of $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ under H_2 also yields $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ when this solution is stirred for 24 h at 25°C. The reaction is accelerated by 355-nm irradiation^{3,4}.

Irradiation (UV) of $\text{Ru}_2(\text{CO})_3(\mu\text{-CHR})(\text{C}_5\text{H}_5\text{-h}^5)_2$ ($\text{R} = \text{H, Me, CO}_2\text{Et}$) in toluene (25°C, 3 d) under H_2 produces $\text{H}_3\text{Ru}_3(\text{CO})_3(\text{C}_5\text{H}_5\text{-h}^5)_3$ in 40–60% yield⁵:



Hydrogen reacts⁶ with $\text{Ru}_3(\text{CO})_8(\text{dppm})_2$ and $\text{Ru}_3(\text{CO})_8(\text{dpam})_2$ ($\text{dpam} = \text{Ph}_2\text{AsCH}_2\text{AsPh}_2$):



The Ru cluster $\text{HRu}_3(\mu\text{-COMe})(\text{CO})_{10}$ reacts^{7,8} with H_2 to produce $\text{H}_3\text{Ru}_3(\mu_3\text{-COMe})(\text{CO})_9$,



The equilibrium constant for reaction (i) is 2.6 in the range 60–80°C in decane⁹.

Hydrogen (1 atm) reacts¹⁰ with $\text{Ru}_3(\text{CO})_{11}[\text{CN}(\text{Bu-t})]$ in refluxing cyclohexane for 1 h to produce $\text{HRu}_3[\mu_3\text{-HCN}(\text{Bu-t})](\text{CO})_9$, along with $\text{HRu}_3[\mu\text{-HCN}(\text{Bu-t})](\text{CO})_8$, $[\text{CN}(\text{Bu-t})]$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12-n}[\text{CN}(\text{Bu-t})]_n$ ($n = 0, 1, 2$). Higher yields of the latter two products are obtained by hydrogenation of $\text{Ru}_3(\text{CO})_{10}[\text{CN}(\text{Bu-t})]$.

Reaction of H_2 with $\text{FeRu}_2(\text{CO})_{12}$ produces² $\text{H}_4\text{Ru}_4(\text{CO})_{12}$. However, $\text{H}_4\text{FeRu}_3(\text{CO})_{12}$ can be prepared from $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ and H_2 in refluxing hexane² or by photolysis³ of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ in a hydrocarbon under H_2 , and $\text{HCoRu}_3(\text{CO})_{13}$ reacts with H_2 in refluxing hexane to produce $\text{H}_3\text{CoRu}_3(\text{CO})_{12}$ in 75% yield¹¹. Stirring $\text{Ru}_2\text{Co}_2(\text{CO})_{13}$ in n-hexane with H_2 for 3 h at 50°C produces $\text{H}_2\text{Ru}_2\text{Co}_2(\text{CO})_{12}$ in 78% yield¹².

(J. TOPICH)

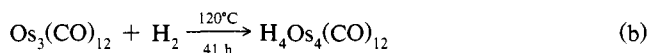
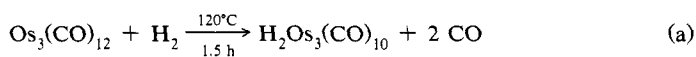
2. S. A. R. Knox, J. W. Keopke, M. A. Andrews, H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
3. H. C. Foley, G. L. Geoffroy, *J. Am. Chem. Soc.*, **103**, 7176 (1981).
4. J. L. Graff, M. S. Wrighton, *Inorg. Chim. Acta*, **63**, 63 (1982).
5. N. J. Forrow, S. A. R. Knox, M. J. Morris, A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 234 (1983).
6. G. Lavigne, N. Lugan, J. J. Bonnett, *Organometallics*, **7**, 1040 (1982).
7. J. B. Keister, *J. Chem. Soc., Chem. Commun.*, 214 (1979).
8. J. B. Keister, M. W. Payne, M. J. Muscatella, *Organometallics*, **2**, 219 (1983).
9. L. M. Bavaro, P. Montangero, J. B. Keister, *J. Am. Chem. Soc.*, **105**, 4977 (1983).
10. M. I. Bruce, R. C. Wallis, *Aust. J. Chem.*, **35**, 709 (1982).
11. W. L. Gladfelter, G. L. Geoffroy, J. C. Calabrese, *Inorg. Chem.*, **19**, 2569 (1980).
12. E. Roland, H. Vahrenkamp, *Organometallics*, **2**, (1983).

1.10.4.3.4. Involving Iron, Osmium, Rhodium, Iridium and Platinum.

The clusters $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$ ($\text{M} = \text{Fe}, \text{Os}$) react^{1,2} with H_2 in refluxing hexane to give $\text{H}_3\text{M}_3(\mu_3\text{-COMe})(\text{CO})_9$. This process can be reversed by reacting the trihydrides with CO. Although $\text{H}_3\text{Fe}_3(\mu_3\text{-COMe})(\text{CO})_9$ is unstable under ambient conditions, the substituted derivative, $\text{H}_3\text{Fe}_3(\mu_3\text{-COMe})(\text{CO})_7(\text{SbPh}_3)_2$, can be obtained by carrying out the hydrogenation in the presence of SbPh_3 .

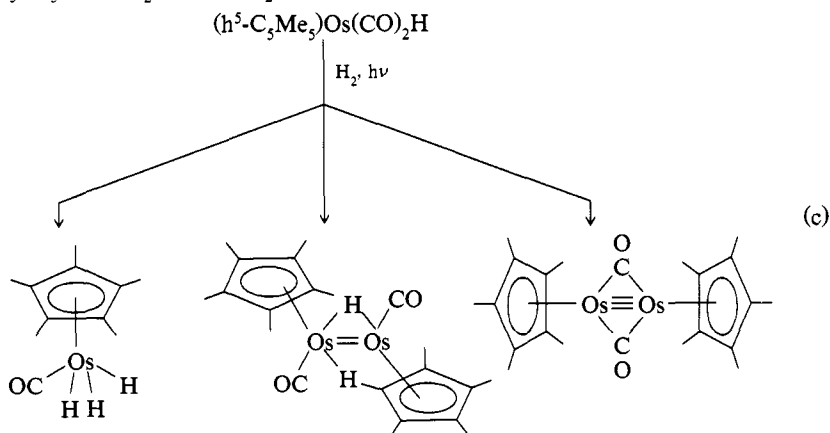
The cluster $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ adds H_2 and loses CO when irradiated³ under H_2 to produce $\text{H}_4\text{FeOs}_3(\text{CO})_{12}$. The product is photosensitive in the presence of H_2 , decomposing to a complex mixture of unidentified compounds.

Hydrogen reacts⁴ with $\text{Os}_3(\text{CO})_{12}$ in n-octane to produce $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{H}_4\text{Os}_4(\text{CO})_{12}$:



When D_2 is bubbled through $\text{Os}_3(\text{CO})_{12}$ for 2 h, exchange occurs with hydrogen from the hydrocarbon solvent.

Photochemically generated 16-electron intermediates are highly reactive. Photolysis⁵ of $(\text{h}^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{H}$ under H_2 produces:



190 1.10. Formation of Bonds between Hydrogen and Transition Metals
 1.10.4. by Oxidative Addition of Hydrogen
 1.10.4.3. to Neutral Species

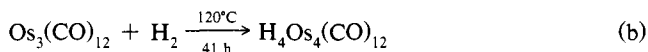
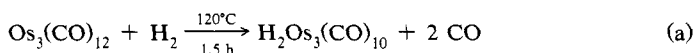
2. S. A. R. Knox, J. W. Keopke, M. A. Andrews, H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
3. H. C. Foley, G. L. Geoffroy, *J. Am. Chem. Soc.*, **103**, 7176 (1981).
4. J. L. Graff, M. S. Wrighton, *Inorg. Chim. Acta*, **63**, 63 (1982).
5. N. J. Forrow, S. A. R. Knox, M. J. Morris, A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 234 (1983).
6. G. Lavigne, N. Lugan, J. J. Bonnett, *Organometallics*, **7**, 1040 (1982).
7. J. B. Keister, *J. Chem. Soc., Chem. Commun.*, 214 (1979).
8. J. B. Keister, M. W. Payne, M. J. Muscatella, *Organometallics*, **2**, 219 (1983).
9. L. M. Bavaro, P. Montangero, J. B. Keister, *J. Am. Chem. Soc.*, **105**, 4977 (1983).
10. M. I. Bruce, R. C. Wallis, *Aust. J. Chem.*, **35**, 709 (1982).
11. W. L. Gladfelter, G. L. Geoffroy, J. C. Calabrese, *Inorg. Chem.*, **19**, 2569 (1980).
12. E. Roland, H. Vahrenkamp, *Organometallics*, **2**, (1983).

1.10.4.3.4. Involving Iron, Osmium, Rhodium, Iridium and Platinum.

The clusters $\text{HM}_3(\mu\text{-COMe})(\text{CO})_{10}$ ($\text{M} = \text{Fe}, \text{Os}$) react^{1,2} with H_2 in refluxing hexane to give $\text{H}_3\text{M}_3(\mu_3\text{-COMe})(\text{CO})_9$. This process can be reversed by reacting the trihydrides with CO. Although $\text{H}_3\text{Fe}_3(\mu_3\text{-COMe})(\text{CO})_9$ is unstable under ambient conditions, the substituted derivative, $\text{H}_3\text{Fe}_3(\mu_3\text{-COMe})(\text{CO})_7(\text{SbPh}_3)_2$, can be obtained by carrying out the hydrogenation in the presence of SbPh_3 .

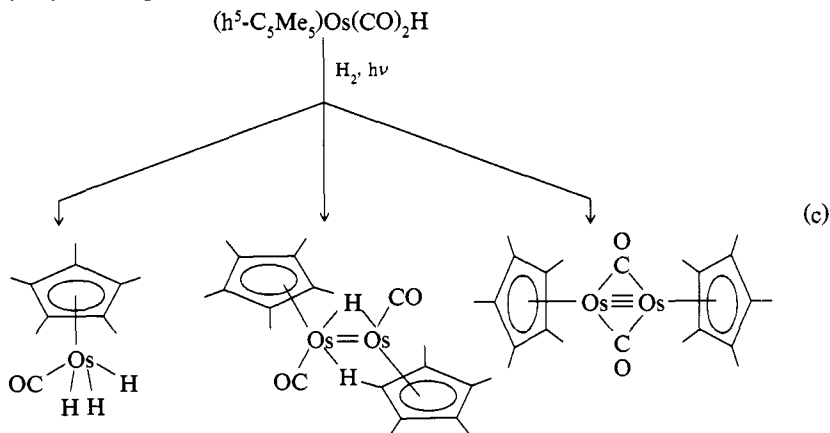
The cluster $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ adds H_2 and loses CO when irradiated³ under H_2 to produce $\text{H}_4\text{FeOs}_3(\text{CO})_{12}$. The product is photosensitive in the presence of H_2 , decomposing to a complex mixture of unidentified compounds.

Hydrogen reacts⁴ with $\text{Os}_3(\text{CO})_{12}$ in n-octane to produce $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{H}_4\text{Os}_4(\text{CO})_{12}$:



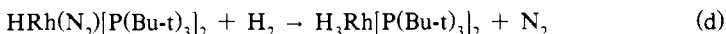
When D_2 is bubbled through $\text{Os}_3(\text{CO})_{12}$ for 2 h, exchange occurs with hydrogen from the hydrocarbon solvent.

Photochemically generated 16-electron intermediates are highly reactive. Photolysis⁵ of $(\text{h}^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{H}$ under H_2 produces:

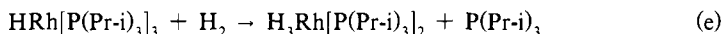


Reaction⁶ of $[(\mu_2\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-NCH}_2\text{CF}_3)]$ with H_2 produces $[\text{H}(\mu_2\text{-H})_3\text{Os}_3(\text{CO})_8(\mu_3\text{-NCH}_2\text{CF}_3)]$ in an oxidative addition of H_2 involving CO loss with incorporation of a terminal and a $\mu_2\text{-H}$ atom into the cluster.

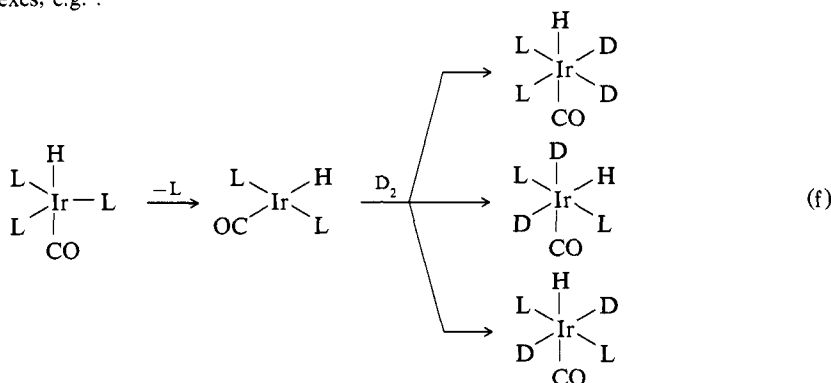
Hydridodinitrogentrialkylphosphine complexes of Rh(I) react⁷:



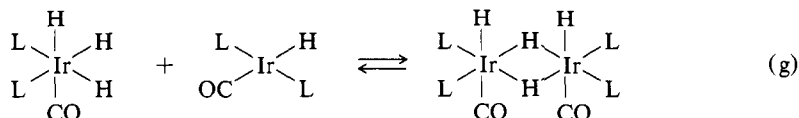
$\text{HRh}(\text{N}_2)[\text{P}(\text{Pr-i})_3]_2$ does not form under the same conditions as its $\text{P}(\text{Bu-t})_3$ analogue, $\text{HRh}[\text{P}(\text{Pr-i})_3]_3$ being formed instead. This Rh(I) hydride will add H_2 with loss of phosphine:



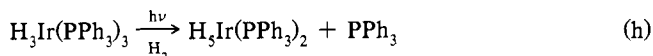
Cis addition is the stereochemical course of the oxidative addition^{8,9} of H_2 to Ir(I) complexes, e.g.⁸:



where $\text{L} = \text{PPh}_3$. Trans addition of D_2 could have occurred, but the H_2 or D_2 addition is cis with H or D scrambling occurring, possibly through a dihydrido-bridged Ir dimer¹⁰:

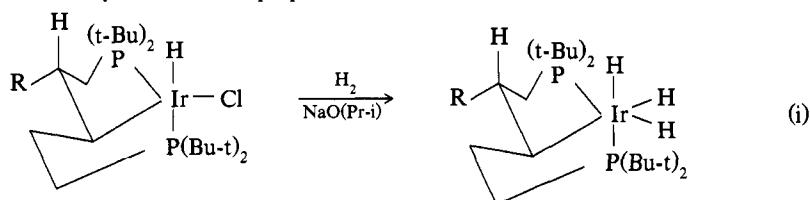


In the photochemistry^{11,12} of the Ir hydride complexes, the primary photochemical process for $\text{H}_3\text{Ir}(\text{PPh}_3)_3$ is loss of H_2 to form $\text{HIr}(\text{PPh}_3)_3$. However, irradiation under H_2 suppresses this pathway and allows another to be observed:



Hydrogen reacts¹³ with $1\text{-}[\text{Ir}(\text{CO})_3(\text{PPh}_3)](7\text{-C}_6\text{H}_5\text{-1,7-B}_{10}\text{C}_2\text{H}_{10})$ in benzene, losing 1 equiv of CO to produce $1\text{-}[\text{H}_2\text{Ir}(\text{CO})_2(\text{PPh}_3)](7\text{-C}_6\text{H}_5\text{-1,7-B}_{10}\text{C}_2\text{H}_{10})$.

Iridium tetrahydrides can be prepared¹⁴:



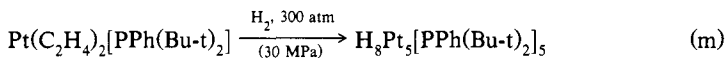
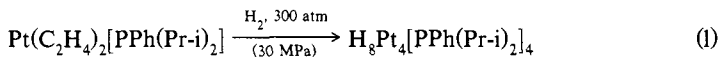
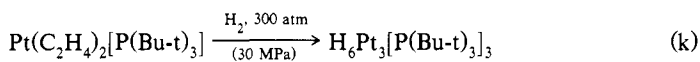
where R = H, Me.

Hydrogen adds¹⁵ to $\text{Pt}[\text{P}(\text{Pr}-i)_3]_3$ to yield $\text{trans-H}_2\text{Pt}[\text{P}(\text{Pr}-i)_3]_2$ with dissociation of 1 equiv of $\text{P}(\text{Pr}-i)_3$. Cis- and trans- H_2PtL_2 (L = PEt_3 , PMe_3) can be prepared by bubbling H_2 (1 atm, 25°C) through $\text{PtL}_2(\text{C}_2\text{H}_4)$ solutions¹⁶.



The ratio of cis and trans isomers formed depends on L and the solvent. The cis isomer has a dipole moment and is better solvated in polar media; hence the relative concentration of cis isomer increases on going from toluene to acetone. In a given solvent the cis geometry is more favored for L = PMe_3 than for L = PEt_3 .

A source of the $\text{Pt}(\text{PR}_3)_2$ fragment is $\text{Pt}(\text{C}_2\text{H}_4)_2\text{PR}_3$. The products of the reaction of $\text{Pt}(\text{C}_2\text{H}_4)_2\text{PR}_3$ with H_2 depend on the phosphine^{17,18}:



(J. TOPICH)

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9. M. Drouin, J. F. Harrod, *Inorg. Chem.*, 22, 999 (1983).
10. R. Crabtree, *Acc. Chem. Res.*, 12, 331 (1979).
11. G. L. Geoffroy, R. Pierantozzi, *J. Am. Chem. Soc.*, 98, 8054 (1976).
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13. B. Longato, S. Bresadola, *Inorg. Chim. Acta*, 33, 189 (1979).
14. R. J. Errington, B. L. Shaw, *J. Organomet. Chem.*, 238, 319 (1982).
15. T. Yoshida, S. Otsuka, *J. Am. Chem. Soc.*, 99, 2134 (1977).
16. R. S. Paonessa, W. C. Troglor, *J. Am. Chem. Soc.*, 104, 1138 (1982).
17. D. Gregson, J. A. K. Howard, M. Murray, J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 716, (1981).
18. P. W. Frost, J. A. K. Howard, J. L. Spencer, D. G. Turner, *J. Chem. Soc., Chem. Commun.*, 1104 (1981).

1.10.4.4. to Cationic Species of Iridium, Rhodium and Platinum with Replacement of Coordinated Ligands.

Oxidative addition of H_2 to cationic metal complexes can occur with replacement of coordinated ligands¹; e.g., $[\text{Ir}(\text{CO})_3\text{L}_2]\text{BPh}_4$ (L = tertiary phosphine or arsine) are prepared² by passing CO through $\text{trans-}[\text{IrCl}(\text{CO})\text{L}_2]$ solutions in the presence of

192 1.10. Formation of Bonds between Hydrogen and Transition Metals

1.10.4. by Oxidative Addition of Hydrogen

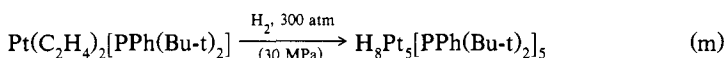
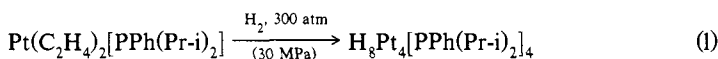
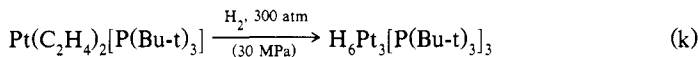
where R = H, Me.

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The ratio of cis and trans isomers formed depends on L and the solvent. The cis isomer has a dipole moment and is better solvated in polar media; hence the relative concentration of cis isomer increases on going from toluene to acetone. In a given solvent the cis geometry is more favored for $\text{L} = \text{PMe}_3$ than for $\text{L} = \text{PET}_3$.

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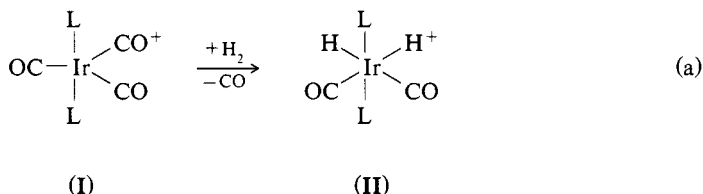
(J. TOPICH)

1. J. B. Keister, *J. Chem. Soc., Chem. Commun.*, 214 (1979).
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17. D. Gregson, J. A. K. Howard, M. Murray, J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 716, (1981).
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1.10.4.4. to Cationic Species of Iridium, Rhodium and Platinum with Replacement of Coordinated Ligands.

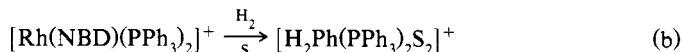
Oxidative addition of H_2 to cationic metal complexes can occur with replacement of coordinated ligands¹; e.g., $[\text{Ir}(\text{CO})_3\text{L}_2]\text{BPh}_4$ ($\text{L} =$ tertiary phosphine or arsine) are prepared² by passing CO through $\text{trans-}[\text{IrCl}(\text{CO})\text{L}_2]$ solutions in the presence of

NaBPh_4 . The cationic dihydrides are obtained in 70–100% yields by bubbling H_2 through $[\text{Ir}(\text{CO})_3\text{L}_2]\text{BPh}_4$ in acetone–methanol at RT:

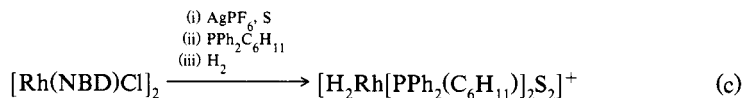


where $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{PMePh}_2, \text{PEtPh}_2, \text{PEt}_2\text{Ph}, \text{PEt}_3, \text{P}(\text{C}_6\text{H}_{11})_3, \text{P}(\text{Pr}-i)_3$. This reaction is reversible, and H_2 is liberated and (I) regenerated by passing CO through the solution. Initial loss of CO occurs for $[\text{Ir}(\text{CO})_3\text{L}_2]^+$, where $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$ or $\text{P}(\text{Pr}-i)_3$, and this is the rate-determining step with H_2 adding to the resulting four-coordinated complex. In the reductive elimination³ of H_2 from $[\text{IrH}_2(\text{CO})_2\text{L}_2]\text{BPh}_4$, the rate decreases: $\text{L} = \text{PPh}_3 > \text{AsPh}_3 > \text{PMePh}_2 > \text{PEtPh}_2 > \text{PEt}_2\text{Ph} > \text{PEt}_3 > \text{P}(\text{C}_6\text{H}_{11})_3 \approx \text{P}(\text{Pr}-i)_3$. The breaking of the metal–hydrogen bonds is the rate-determining step and is related to the strength of the metal–hydrogen bond in each complex. The Ir(III) complexes are stabilized toward reductive elimination by the more basic phosphines.

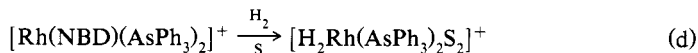
Cationic Rh hydrides⁴ can be isolated:



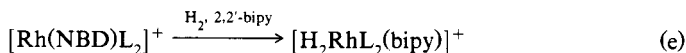
where S = acetone, ethanol, CH_3CN ; NBD = norbornadiene:



where S = acetone, CH_3CN ;



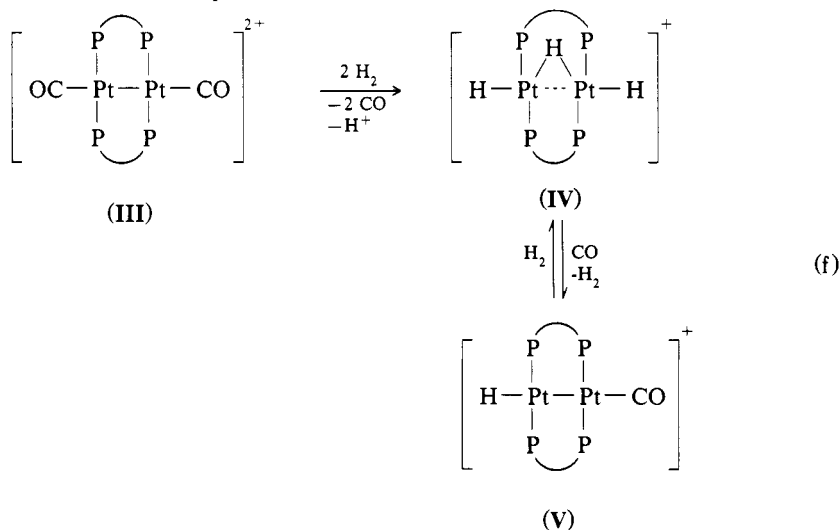
where S = acetone, CH_3CN ;



where $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{AsPh}_3$ and 2,2'-bipyridine (bipy). Reaction of $[\text{Rh}(\text{NBD})\text{L}_2]^+$ with H_2 yields a transient intermediate, $[\text{H}_2\text{Rh}(\text{NBD})\text{L}_2]^+$. Hydride transfer yields norbornene, which may dissociate before it is reduced to norbornane. On reduction of NBD, solvent or other ligand occupies the vacated coordination sites.

Cationic olefin complexes of Ir(I) are also susceptible to loss of coordinated ligands on oxidative addition of H_2 ; e.g., $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]\text{BF}_4$ (S = solvent) is prepared⁵ from $[\text{Ir}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$ (COD = 1,5-cyclooctadiene) and H_2 at 0–20°C in Me_2CO , MeCN, tetrahydrofuran (THF), MeOH, EtOH, i-PrOH, t-BuOH and H_2O . The ease of solvent displacement from $[\text{IrH}_2\text{S}_2(\text{PPh}_3)_2]^+$ follows the order⁵: $\text{H}_2\text{O} \approx \text{THF} > \text{t-BuOH} > \text{i-PrOH} > \text{Me}_2\text{CO} > \text{EtOH} > \text{MeOH} > \text{MeCN}$.

For binuclear Pt complexes^{6,7}:



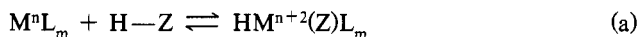
where $(\text{PP} = \text{Ph}_2\text{PCH}_2\text{PPh}_2)$. Displacement of H_2 from (IV) by CO is readily reversible, so treatment of (V) with xs H_2 produces (IV) in good yield.

(J. TOPICH)

1. H. D. Kaesz, R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
2. M. J. Church, M. J. Mays, R. N. F. Simpson, F. P. Stefanini, *J. Chem. Soc., A*, 2909 (1970).
3. M. J. Mays, R. N. F. Simpson, F. P. Stefanini, *J. Chem. Soc., A*, 3000 (1970).
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1.10.5. by Oxidative Addition to Metal Complexes

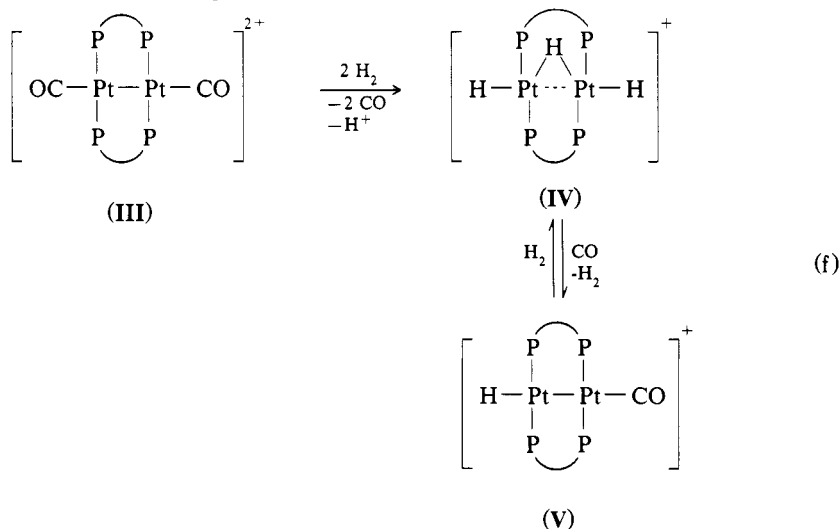
Reviews of oxidative addition to d^8 -transition metals¹ and transition metals in general², including the formation of hydrogen-metal bonds³, are available. Hydrogen-element bonds add to metals predominantly to the left in the transition-metal series. This is a formal $2 e^-$ oxidation of the metal by transfer of electron density to the proton. Therefore, the reaction is oxidative addition and the reverse reaction is reductive elimination:



with no mechanistic information implied⁴. Mechanisms may be concerted or stepwise with either the hydrogen or the element adding first⁵. Oxidative addition to a metal complex requires nonbonding electron density on the metal, two vacant coordination sites and a metal with oxidation states separated by two units. Both the hydrogen and

194 1.10. Formation of Bonds between Hydrogen and Transition Metals

For binuclear Pt complexes^{6,7}:



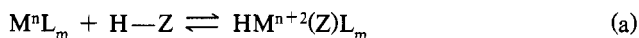
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1.10.5. by Oxidative Addition to Metal Complexes

Reviews of oxidative addition to d^8 -transition metals¹ and transition metals in general², including the formation of hydrogen-metal bonds³, are available. Hydrogen-element bonds add to metals predominantly to the left in the transition-metal series. This is a formal $2 e^-$ oxidation of the metal by transfer of electron density to the proton. Therefore, the reaction is oxidative addition and the reverse reaction is reductive elimination:



with no mechanistic information implied⁴. Mechanisms may be concerted or stepwise with either the hydrogen or the element adding first⁵. Oxidative addition to a metal complex requires nonbonding electron density on the metal, two vacant coordination sites and a metal with oxidation states separated by two units. Both the hydrogen and

element bond are coordinated to the metal in the product such that the overall charge on the metal complex is unchanged. This is in contrast to the protonation of metal complexes discussed in §1.10.6. The tendency of a metal complex to undergo oxidative addition parallels its basicity. Basicity increases on descending a transition-metal triad, by decreasing metal oxidation state and with the increase of electron-donating ligands in the complex.

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When anhyd HCl is bubbled through trans-IrCl(CO)(PPh₃)₂ in ether, the O_h product HIrCl(CO)(PPh₃)₂ is formed rapidly and quantitatively. In nonpolar solvents or in the solid state the cis isomer is obtained. In polar solvents mixtures of cis and trans adducts form³. When the phosphine is tri-*o*-tolylphosphine, HX addition to trans-IrCl(CO)(PR₃)₂ is slow because the apical sites are blocked⁴. When the sterically bulky but strongly basic tricyclohexylphosphine is incorporated into trans-IrCl(CO)(PR₃)₂, the HCl adduct is formed easily⁵. Moreover, when the phosphine of the complex is PMe₂(*o*-MeOC₆H₄), interaction of the methoxy oxygen with the Ir center increases its nucleophilicity and so facilitates oxidative addition⁶.

With non-phosphorus-containing ligands, e.g., Ir(Oq)(CO)(PPh₃) (Oq = 8-oxyquinolate), when dry HCl is added in 1 min HIrCl(Oq)(CO)(PPh₃) (82%) forms⁷. Addition of HCl, HBr and HI to the carborane—Ir complexes, trans-Ir(carborane)(CO)PR₃, occurs in both the solid state and solution⁸. The stereochemistry of the adducts HIrX(carborane)(CO)PR₃ depends on the medium and the carborane ligand. The adducts reductively eliminate H-carborane on heating in benzene. Indirect addition of HCl to an Ir complex occurs between [Ir(dppe)₂]Cl where dppe is 1,2[(C₆H₅)₂P]₂CH₂-CH₂ and B₁₀H₁₃X (X = H or 6-Cl) which yields [IrHCl(dppe)₂][B₁₀H₁₂X] (74%)⁹. The cyclometallated tetrahydride H₄Ir(t-Bu₂PCH₂CH₂CHCH₂CH₂PBu-t₂) is formally reduced by HBr, producing HIrBr(t-Bu₂PCH₂CH₂CHCH₂CH₂PBu-t₂)¹⁰.

Reviews of synthetic methods to hydrido-Ni, -Pd and -Pt, including oxidative addition of hydrogen halides, are available^{11,12}.

Two-, three- and four-coordinated Pd(0) complexes react with HCl to form trans-HPdCl(PR₃)₂. The two-coordinated complexes, Pd(PBu-t₃)₂ and Pd(PPhBu-t₂)₂, react¹³ with HCl at RT quantitatively, whereas the higher coordinated complexes, Pd(PMe₃)₄, Pd(PMePh₂)₄ and Pd(Pi-Pr₃)₃, react¹⁴ at -50°C. Similarly, HPtCl[PPh(Bu-t₂)]₂ is prepared almost quantitatively at RT from HCl and Pt[PPh(Bu-t₂)]₂ in *n*-hexane¹³. The

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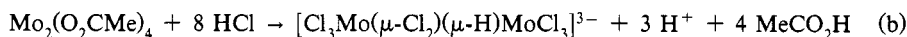
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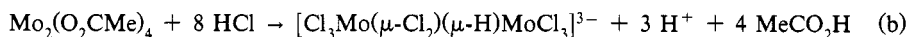
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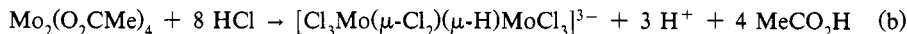
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1.10.5.2. of Hydrogen-Boron Bonds.

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The most explicit oxidative additions of B—H bonds to metal centers involve Ir complexes, e.g., the o-metallation of a B—H bond obtained³ with $[\text{Ir}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$ and xs 1-(Me_2P)-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ in cyclohexane at reflux for 2 h under N_2 in quantitative yield. The product is $\text{HIrCl}(\text{C}_2\text{B}_{10}\text{H}_{10}\text{PMe}_2)(\text{C}_2\text{B}_{10}\text{H}_{11}\text{PMe}_2)_2$. The hydride ligand originates from a boron of the carborane cage (by deuterium labeling). The intermolecular conversion occurs⁴ between $\text{IrCl}(\text{PPh}_3)_2$ and 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ at reflux in cyclohexane for 1 h. The five-coordinated complex, 3- $[\text{HIrCl}(\text{PPh}_3)_2]$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$, is isolated in > 90% yield. The 1,12-carborane isomer of the above Ir complex catalyzes deuterium-hydrogen exchange in 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$. The isolated metallocarboranes are, therefore, models for intermediates in this exchange. Pentaborane, B_5H_9 , is oxidatively added⁵ to $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$ but not to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. This demonstrates the increased basicity of the trimethylphosphine-Ir complex, which decomposes slowly at 25°C but can be kept indefinitely at -20°C.

Several Ir—B bonds form in the same complex⁶ from $\text{Ti}(\text{B}_3\text{H}_8)$ with trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ when stirred in benzene at 20°C for 48 h. The product is an O_h -borallyl compound (by ¹H and ¹¹B NMR) containing one two-electron, two-center Ir—B bond and one two-electron, three-center Ir—B₂ bond, $\mu^3\text{-B}_3\text{H}_7\text{IrH}(\text{CO})(\text{PPh}_3)_2$.

Reactions of the anion $[\text{B}_3\text{H}_8]^-$ with other transition-metal complexes do not lead to metal-boron bonds. The borane anion acts as a bidentate ligand with bonding to the metal only through hydrogen⁷, but this type of metal-hydrogen-boron interaction can transform to direct metal-boron bonding. When $\text{Fe}_2(\text{B}_2\text{H}_6)(\text{CO})_6$ is treated with $\text{Fe}_2(\text{CO})_9$ in pentane at 25°C for 7 h, the diborane moiety oxidatively adds to yield $\text{HFe}_4(\text{BH}_2)(\text{CO})_{12}$, which consists of an Fe_4 butterfly structure and a BH_2 fragment bonded to all four Fe atoms⁸.

When CoCl_2 , NaC_5H_5 and B_5H_9 react at -78°C overnight, metalloboranes result, but only in low yield⁹. Two of these contain both Co—H and Co—B bonds¹⁰.

A less straightforward example of oxidative addition of a B—H bond to a metal is the reaction¹¹ of $\text{Ru}_3(\text{CO})_{12}$ with NaBH_4 . One of the five products isolated is formulated as $\text{HRu}_4(\text{BH}_2)(\text{CO})_{12}$.

(T. J. LYNCH)

1. C. E. Housecroft, T. P. Fehlner, *Adv. Organomet. Chem.*, **21**, 57 (1982).
2. N. N. Greenwood, *Pure Appl. Chem.*, **55**, 1415 (1983).
3. E. L. Hoel, M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 2712 (1973).
4. E. L. Hoel, M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 6770 (1974).
5. M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, S. S. Wreford, *J. Am. Chem. Soc.*, **96**, 4041 (1974).
6. N. N. Greenwood, J. D. Kennedy, D. Reed, *J. Chem. Soc., Dalton Trans.*, 196, (1980).
7. D. F. Gaines, S. J. Hildebrandt, *Inorg. Chem.*, **17**, 794 (1978).
8. K. S. Wong, W. R. Scheidt, T. P. Fehlner, *J. Am. Chem. Soc.*, **104**, 1111 (1982).
9. V. R. Miller, R. Weiss, R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 5646 (1977).
10. J. R. Pipal, R. N. Grimes, *Inorg. Chem.*, **16**, 3251, 3255 (1977).
11. C. R. Eady, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.*, 477, (1977).

1.10.5.3. of Hydrogen-Carbon Bonds.

Oxidative addition of H—C bonds to transition metals, which also is referred to as an activation of the H—C bond, is of scientific and technological importance.¹⁻⁷ (See §1.10.2 for activation of H—C bonds by metal-atom vapors.) Intramolecular oxidative addition of H—C bonds (cyclometallation) occurs, but organic functional

1.10. Formation of Bonds between Hydrogen and Transition Metals 197

1.10.5. by Oxidative Addition to Metal Complexes

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(T. J. LYNCH)

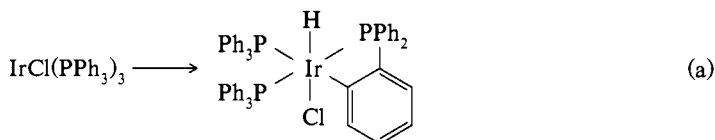
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4. E. L. Hoel, M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 6770 (1974).
5. M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, S. S. Wreford, *J. Am. Chem. Soc.*, **96**, 4041 (1974).
6. N. N. Greenwood, J. D. Kennedy, D. Reed, *J. Chem. Soc., Dalton Trans.*, 196, (1980).
7. D. F. Gaines, S. J. Hildebrandt, *Inorg. Chem.*, **17**, 794 (1978).
8. K. S. Wong, W. R. Scheidt, T. P. Fehlner, *J. Am. Chem. Soc.*, **104**, 1111 (1982).
9. V. R. Miller, R. Weiss, R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 5646 (1977).
10. J. R. Pipal, R. N. Grimes, *Inorg. Chem.*, **16**, 3251, 3255 (1977).
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groups undergo intermolecular H—C oxidative additions to metal complexes less commonly.

The rates of intramolecular oxidative addition of aromatic H—C bonds⁸:



(cyclometallation) can be increased by Li-2H-1,2-B₁₀C₂H₁₀⁹ or Li alkyls or aryls¹⁰. Aliphatic H—C bonds also are activated toward intramolecular oxidative addition when bound to a phosphine ligand. When RhCl₃ · 3 H₂O is treated with the long-chain diphosphine t-Bu₂PCH₂CH₂CH₂CH₂CH₂PBu-t₂, the product¹¹ is [HRhCl[t-Bu₂PCH₂CH₂CH₂CH₂CH₂PBu-t₂]] formed by oxidative addition of the middle H—C bond. Further dehydrogenation leads to [RhCl[t-Bu₂PCH₂CH₂CH=CHCH₂PBu-t₂]], in which the olefin and trans-phosphorus atoms are bound to the Rh center. A second H—C bond cleavage from the same middle carbon atom of a similar Ir complex forms an Ir-coordinated carbene¹². In related complexes with similar ligands the cleavage of three H—C bonds yields π-allyl complexes¹³. Polynuclear Os complexes induce H—C bond oxidative addition with organic ligands^{14–16}.

Intermolecular oxidative addition of H—C usually involves activated H—C bonds. The weak acid HCN reacts with transition-metal complexes; e.g., HCN and NiL₄ lead to the hydride complexes HNi(CN)L₃ (L = various phosphorus ligands)¹⁷. The versatile complex IrCl(CO)(PPh₃)₂ adds HCN cleanly in CH₂Cl₂ at RT to form¹⁸ HIr(CN)(Cl)(PPh₃)₂. The zero-valent complexes Pt(PPh₃)₄ or Pt(PPh₃)₃ also add HCN to yield¹⁹ HPt(CN)(PPh₃)₂. Reactions of HMNp(dmpe)₂ (M = Fe, Ru, Os; Np = 2-naphthyl; dmpe = Me₂PCH₂CH₂PMe₂) with HCN and terminal acetylenes give HMR(dmpe)₂ that contain new M—C bonds (R = —CN, —C₂R')²⁰.

Terminal alkyne H—C bonds add to Pt(PPh₃)₃; e.g., the reaction with 1-ethynylcyclohexanol gives²¹ the trans-dihydride, H₂Pt(CCR)₂(PPh₃)₂. Metal vapors of Yb, Sm and Er react with 1-hexyne, and the first step is oxidative addition of the terminal H—C bond²².

Through the oxidative addition of aldehydes, hydridoformyl and -acyl compounds are formed. Formaldehyde adds to the reactive complex, [Ir(PMe₃)₄]PF₆, to afford²³ [HIr(CHO)(PMe₃)₄]PF₆. Cyclometallation of an aldehyde H—C bond results from treating RhCl(PPh₃)₃ with 8-quinolinecarboxaldehyde in CH₂Cl₂ in 10 min to yield (95%) HRh(CRO)Cl(PPh₃)₂ (R = 8-carboxyquinoline)²⁴.

The sterically crowded Pt[P(C₆H₁₁)₃]₂ reacts with fluorobenzenes such as C₆HF₅ to afford²⁵ HPt(C₆F₅)[P(C₆H₁₁)₃]₂.

Cyclopentadiene reacts with transition metals by oxidative addition of one H—C bond at the saturated carbon. Metal-atom vapors of Mo and W codeposit with cyclopentadiene to form²⁶ (h⁵-C₅H₅)₂MH₂. Irradiation of Mo(CO)₆ with cyclopentadiene in isooctane yields²⁷ (h⁵-C₅H₅)Mo(CO)₂C₅H₇-h³)²⁸ that involves overall H transfer between ligands.

The H—C bond cleavage in saturated hydrocarbons is only realized in low-T matrices and in homogeneous solution. Reactions of methane and ethane with Ni are calculated theoretically²⁸. Metals (Mn, Fe, Co, Cu, Zn, Ag and Au) in CH₄ matrices insert into the H—C bonds when irradiated at 15K to form²⁹ HMCH₃.

Cyclopentane reacts with $[\text{IrH}_2\text{S}_2(\text{PPh}_3)]^+ [\text{S} = \text{H}_2\text{O}, (\text{CH}_3)_2\text{CO}]$ at 80°C in the presence of 3,3-dimethyl-1-butene, which acts as a hydrogen acceptor, to yield³⁰ $[\text{IrH}(\text{C}_5\text{H}_5\text{-h}^5)(\text{PPh}_3)_2]^+$. Another Ir complex, $\text{H}_2\text{Ir}(\text{C}_5\text{Me}_5\text{-h}^5)(\text{PMe}_3)_3$, when irradiated in cyclohexane or neopentane at RT yields $\text{HIrR}(\text{C}_5\text{Me}_5\text{-h}^5)(\text{PMe}_3)$ ($\text{R} = \text{cyclohexyl}$, neopentyl, respectively)³¹. Irradiation of $\text{Ir}(\text{C}_5\text{Me}_5\text{-h}^5)(\text{CO})_2$ in cyclohexane or neopentane at RT forms the hydridoalkyl addition products $\text{HIrR}(\text{C}_5\text{Me}_5\text{-h}^5)(\text{CO})$ ($\text{R} = \text{cyclohexyl}$, neopentyl)³². The mechanism and thermodynamics of alkane and arene $\text{H}-\text{C}$ bond activation³³ for the alkyl- and aryl-hydride complexes, $\text{HRhR}(\text{C}_5\text{Me}_5\text{-h}^5)(\text{PMe}_3)$ ($\text{R} = \text{Me}, \text{Ph}$) are known.

Chlorination of CH_4 is catalyzed by supported Rh complexes involving $\text{H}-\text{C}$ activation of CH_4 methane by the metal³⁴. Methane exchanges with $\text{La}-\text{CH}_3$ complexes³⁵

(T. J. LYNCH)

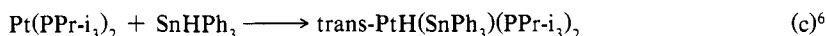
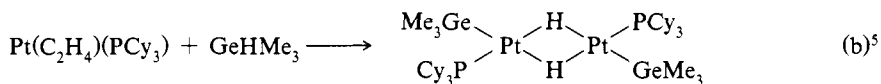
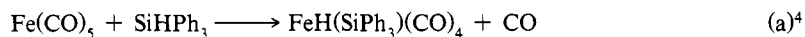
1. E. L. Muetterties, *Chem. Soc. Rev.*, **11**, 283 (1982).
2. G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
3. D. E. Webster, *Adv. Organomet. Chem.*, **15**, 147 (1977).
4. G. W. Parshall, D. L. Thorn, T. H. Tulip, *ChemTech.*, 571 (1982).
5. R. Dagani, *Chem. Eng. News*, **60**, 59 (18 Jan., 1982).
6. J. P. Collman, L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1980, p. 211.
7. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, 1980, p. 1244.
8. M. A. Bennett, D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
9. S. Bresadola, B. Longato, F. Morandini, *Inorg. Chim. Acta*, **25** L135 (1977).
10. K. V. Deuten, L. Dahlenburg, *Cryst. Struct. Commun.*, **9**, 421 (1980).
11. C. Crocker, R. J. Errington, R. Markham, C. J. Moulton, K. J. Odell, B. J. Shaw, *J. Am. Chem. Soc.*, **102**, 4373 (1980).
12. H. D. Empsall, E. M. Hyde, R. Markham, W. S. McDonald, M. C. Norton, B. L. Shaw, B. Weeks, *J. Chem. Soc., Chem. Commun.*, 589 (1977).
13. M. A. Bennett, H. Neumann, *Aust. J. Chem.*, **33**, 1251 (1980).
14. J. R. Shapley, D. E. Samkoff, C. Bueno, M. R. Churchill, *Inorg. Chem.*, **21**, 634 (1982), and refs. therein.
15. C. C. Yin, A. J. Deeming, *J. Organomet. Chem.*, **133**, 123 (1977).
16. A. J. Deeming, M. Underhill, *J. Chem. Soc., Dalton Trans.*, 2727 (1973).
17. J. D. Druliner, A. D. English, J. P. Jesson, P. Meakin, C. A. Tolman, *J. Am. Chem. Soc.*, **98**, 2156 (1976).
18. H. Singer, G. Wilkinson, *J. Chem. Soc., A*, 2516 (1968).
19. F. Cariati, R. Ugo, F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).
20. S. D. Ittel, C. A. Tolman, A. D. English, J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 7577 (1978).
21. D. M. Roundhill, in *Transition Metal Hydrides*, R. Bau, ed., Advances in Chemistry Series No. 167, American Chemical Society, Washington, DC, 1978, p. 160.
22. W. J. Evans, S. C. Engerer, K. M. Coleson, *J. Am. Chem. Soc.*, **103**, 6672 (1981).
23. D. L. Thorn, *Organometallics*, **1**, 197 (1982).
24. J. W. Suggs, *J. Am. Chem. Soc.*, **100**, 640 (1978).
25. J. Fornies, M. Green, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1006 (1977).
26. E. M. Van Dam, W. N. Brent, M. P. Silvon, P. S. Skell, *J. Am. Chem. Soc.*, **97**, 465 (1975).
27. W. C. Mills, III, M. S. Wrighton, *J. Am. Chem. Soc.*, **101**, 5830 (1979).
28. M. R. A. Blomberg, U. Brandemark, P. E. M. Siegbahn, *J. Am. Chem. Soc.*, **105**, 5557 (1983).
29. W. E. Billups, M. M. Konarski, R. H. Hauge, J. L. Margrave, *J. Am. Chem. Soc.*, **102**, 7393 (1980).
30. R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, J. M. Quirk, *J. Am. Chem. Soc.*, **104**, 107 (1982).
31. A. H. Janowicz, R. G. Bergman, *J. Am. Chem. Soc.*, **104**, 352 (1982).
32. J. K. Hoyano, W. A. G. Graham, *J. Am. Chem. Soc.*, **104**, 3723 (1982).
33. W. D. Jones, F. J. Feher, *J. Am. Chem. Soc.*, **106**, 1650 (1984).

34. N. Kitajima, J. Schwartz, *J. Am. Chem. Soc.*, **106**, 2220 (1984).

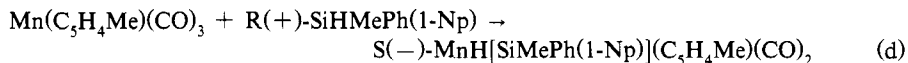
35. P. L. Watson, *J. Am. Chem. Soc.*, **105**, 6491 (1983).

1.10.5.4. of Hydrogen—Other Group IVB Element Bonds.

Oxidative addition of the H—Si bond is the most studied of the group IVB elements with the exception of carbon because of its relation to the industrially important catalytic hydrosilation of alkenes, alkynes and ketones¹. Compounds containing the Si—M bond are stable. While they are also synthesized by routes other than oxidative addition of the H—Si bond^{2,3}. H—Si, H—Ge and H—Sn add to transition metals:



where Cy = cyclohexyl. The stereochemistry of the oxidative addition at Si using an optically active silane proceeds with retention of configuration^{7,8}:



where Np = naphthyl.

Oxidative addition of H—Si bonds to metals with concomitant loss of CO is performed photochemically as in Eq. (d). The silyl hydride, *cis*-HRe(SiPh₃)(C₅H₅-h⁵)-(CO)₂, is obtained in 15% yield by UV irradiation⁹ of (h⁵-C₅H₅)Re(CO)₃ with HSiPh₃ in cyclohexane for 7 h. Triphenylsilane with Rh(C₅H₅-h⁵)(CO)₂ yields HRh(SiPh₃)-(C₅H₅-h⁵)(CO) also under irradiation in nonpolar solvents¹⁰. The anion [Mn(CO)₅][−], when photolyzed in the presence of HSiPh₃, results in high yields of the oxidative-addition product,¹¹ [HMn(SiPh₃)(CO)₄][−]. A formal Ir³⁺ to Ir⁵⁺ oxidative addition occurs in the reaction of Ir₂(μ-H₂)(C₅Me₅-h⁵)₂Cl₂ with two SiHEt₃ to form¹² two H₂Ir(SiEt₃)-(C₅Me₅-h⁵)Cl. When the Ru or Os clusters, M₃(CO)₁₂, are treated with HSiCl₃ at 75°C or 135°C, respectively, in hexane, three equiv of the silane add to the clusters to afford M₃(μ-H)₃(SiCl₃)₃(CO)₉ (M = Ru, 48%; Os, 62%)¹³.

(T. J. LYNCH)

1. J. L. Speier, *Adv. Organomet. Chem.*, **17**, 407 (1979).

2. C. S. Cundy, B. M. Kingston, M. F. Lappert, *Adv. Organomet. Chem.*, **17**, 407 (1979).

3. R. J. P. Corriu, E. Colomer, *Ann. Chim. (Paris)*, **8**, 121 (1983).

4. W. Jetz, W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).

5. M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, C. A. Tsipis, *J. Chem. Soc., Chem. Commun.*, 671 (1976).

6. H. C. Clark, A. B. Goel, C. Billard, *J. Organomet. Chem.*, **182**, 431 (1979).

7. E. Colomer, R. J. P. Corriu, A. Vioux, *J. Chem. Soc., Chem. Commun.*, 175 (1976).

8. E. Colomer, R. J. P. Corriu, A. Vioux, *Inorg. Chem.*, **18**, 695 (1979).

9. D. F. Dong, J. K. Hoyano, W. A. G. Graham, *Can. J. Chem.*, **59**, 1455 (1981).

10. A. J. Oliver, W. A. G. Graham, *Inorg. Chem.*, **10**, 1 (1971).

11. R. A. Faltynek, M. S. Wrighton, *J. Am. Chem. Soc.*, **100**, 2702 (1978).

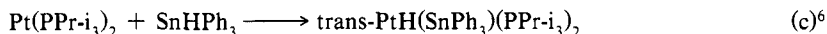
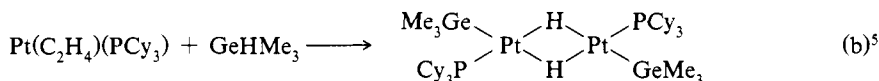
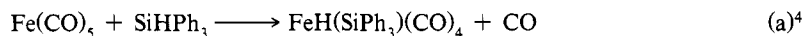
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34. N. Kitajima, J. Schwartz, *J. Am. Chem. Soc.*, **106**, 2220 (1984).

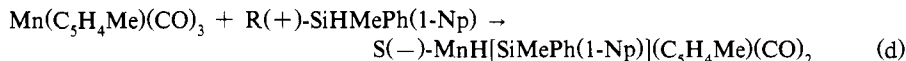
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Oxidative addition of H—Si bonds to metals with concomitant loss of CO is performed photochemically as in Eq. (d). The silyl hydride, *cis*-HRe(SiPh₃)(C₅H₅-h⁵)(CO)₂, is obtained in 15% yield by UV irradiation⁹ of (h⁵-C₅H₅)Re(CO)₃ with HSiPh₃ in cyclohexane for 7 h. Triphenylsilane with Rh(C₅H₅-h⁵)(CO)₂ yields HRh(SiPh₃)(C₅H₅-h⁵)(CO) also under irradiation in nonpolar solvents¹⁰. The anion [Mn(CO)₅][−], when photolyzed in the presence of HSiPh₃, results in high yields of the oxidative-addition product,¹¹ [HMn(SiPh₃)(CO)₄][−]. A formal Ir³⁺ to Ir⁵⁺ oxidative addition occurs in the reaction of Ir₂(μ-H₂)(C₅Me₅-h⁵)₂Cl₂ with two SiHET₃ to form¹² two H₂Ir(SiEt₃)(C₅Me₅-h⁵)Cl. When the Ru or Os clusters, M₃(CO)₁₂, are treated with HSiCl₃ at 75°C or 135°C, respectively, in hexane, three equiv of the silane add to the clusters to afford M₃(μ-H)₃(SiCl₃)₃(CO)₉ (M = Ru, 48%; Os, 62%)¹³.

(T. J. LYNCH)

1. J. L. Speier, *Adv. Organomet. Chem.*, **17**, 407 (1979).

2. C. S. Cundy, B. M. Kingston, M. F. Lappert, *Adv. Organomet. Chem.*, **17**, 407 (1979).

3. R. J. P. Corriu, E. Colomer, *Ann. Chim. (Paris)*, **8**, 121 (1983).

4. W. Jetz, W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).

5. M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, C. A. Tsipis, *J. Chem. Soc., Chem. Commun.*, 671 (1976).

6. H. C. Clark, A. B. Goel, C. Billard, *J. Organomet. Chem.*, **182**, 431 (1979).

7. E. Colomer, R. J. P. Corriu, A. Vioux, *J. Chem. Soc., Chem. Commun.*, 175 (1976).

8. E. Colomer, R. J. P. Corriu, A. Vioux, *Inorg. Chem.*, **18**, 695 (1979).

9. D. F. Dong, J. K. Hoyano, W. A. G. Graham, *Can. J. Chem.*, **59**, 1455 (1981).

10. A. J. Oliver, W. A. G. Graham, *Inorg. Chem.*, **10**, 1 (1971).

11. R. A. Faltynek, M. S. Wrighton, *J. Am. Chem. Soc.*, **100**, 2702 (1978).

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The H-O bonds of water, alcohols and carboxylic acids oxidatively add to metal complexes. Water reacts with the zero-valent Pt complex, $\text{Pt[P(Pr-}i)_3]_2$; with an xs of H_2O in tetrahydrofuran (THF), $\text{HPt(OH)[P(Pr-}i)_3]_2$ is formed in 0.5 h in 18% yield¹. The compound is thermally unstable but can be stored for several weeks at $<0^\circ\text{C}$. Heating $\text{Os}_3(\text{CO})_{12}$ and H_2O to 230°C in a sealed and evacuated vessel leads to polynuclear complexes, one of which is the double edge-bridged cluster $\text{HOs}_3(\text{OH})(\text{CO})_{10}$ in 2% yield^{2,3}. A 71% yield of this compound³ is isolated by column chromatography by treating $\text{Os}_3(\text{NCMe})_2(\text{CO})_{10}$ with xs H_2O in THF for 0.5 h. The Ru analogue, $\text{Ru}_3(\text{CO})_{12}$ forms only hydrides without the -OH group². The product from electrochemical reduction⁴ of aq $[\text{trans-}[\text{Rh(en)}_2\text{Cl}_2]]^+$ (where en = ethylenediamine) under Ar is $[\text{trans-}[\text{Rh(en)}_2\text{H(OH)}]]^+$.

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Alcohols are used in the synthesis of metal hydrides⁹ where metal alkoxides are intermediates¹⁰. Isolation of hydridometal alkoxides from the oxidative addition of alcohols to metal centers is not common. Hydrocarbon solns of $\text{W}_2(\text{NMe}_2)_6$ and 2-propanol generate¹¹ NHMe_2 and H_2 at RT. The product results from alcoholysis, oxidative addition of $i\text{-PrOH}$ and condensation to the tetramer, $\text{H}_2\text{W}_4(\text{OPr-}i)_{14}$. Both $\text{Os}_3(\text{CO})_{12}$ ³ and $\text{Os}_3(\text{NCMe})_2(\text{CO})_{10}$ ¹² oxidatively add HOR (R = Me, Et), forming $\text{HOs}_3(\text{OR})(\text{CO})_{10}$. Phenol adds¹³ to $\text{Ni[P(C}_6\text{H}_{11})_3]_2$ under mild conditions to yield $\text{HNi(OPh)[P(C}_6\text{H}_{11})_3]_2$.

Carboxylic and sulfonic acids react with low-valent metal complexes, forming metal hydrides. Reactions of the two-coordinated complexes PdL_2 [$\text{L} = \text{P(Bu-}t)_3$, $\text{PPh(Bu-}t)_2$] and $\text{Pt[PPh(Bu-}t)_2]$ with HOCOCF_3 produces $\text{trans-HM(OCOCF}_3)_2$ (M = Pd, Pt)¹⁴. The three-coordinated $\text{Pd(PPr-}i)_3$ also reacts with HOCOCF_3 to yield $\text{trans-HPd(OCOCF}_3)_2$. The complex $\text{HPt(OCOCF}_3)_2[\text{As(Bu-}t)_3]_2$ is prepared in 96% yield¹⁵ in 40 min by combining $\text{HPt}_2[\text{As(Bu-}t)_3]_2$ and HOCOCF_3 in hexane at RT. The sulfonic acids, HOSO_2CF_3 and $\text{HOSO}_2\text{C}_4\text{F}_{11}$ react with $\text{Ir(L)Cl(PPh}_3)_2$ (L = CO, N_2) leading to the O_h $\text{HIr(X)(L)Cl(PPh}_3)_2$ (X = OSOCF_3 , $\text{OSOC}_4\text{F}_{11}$)¹⁶.

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Carboxylic and sulfonic acids react with low-valent metal complexes, forming metal hydrides. Reactions of the two-coordinated complexes PdL_2 [$\text{L} = \text{P}(\text{Bu-}t)_3$, $\text{PPh}(\text{Bu-}t)_2$] and $\text{Pt}[\text{PPh}(\text{Bu-}t)_2]$ with HOCOFCF_3 produces $\text{trans-HM}(\text{OCOFCF}_3)_2$ ($\text{M} = \text{Pd}, \text{Pt}$)¹⁴. The three-coordinated $\text{Pd}(\text{PPr-}i)_3$ also reacts with HOCOFCF_3 to yield $\text{trans-HPd}(\text{OCOFCF}_3)(\text{PPr-}i)_2$. The complex $\text{HPt}(\text{OCOFCF}_3)[\text{As}(\text{Bu-}t)_3]_2$ is prepared in 96% yield¹⁵ in 40 min by combining $\text{HPt}_2[\text{As}(\text{Bu-}t)_3]_2$ and HOCOFCF_3 in hexane at RT. The sulfonic acids, HOSO_2CF_3 and $\text{HOSO}_2\text{C}_4\text{F}_{11}$ react with $\text{Ir}(\text{L})\text{Cl}(\text{PPh}_3)_2$ ($\text{L} = \text{CO}, \text{N}_2$) leading to the O_h $\text{HIr}(\text{X})(\text{L})\text{Cl}(\text{PPh}_3)_2$ ($\text{X} = \text{OSOFCF}_3, \text{OSOC}_4\text{F}_{11}$)¹⁶.

Formic acid adds to the lightly stabilized cluster, $\text{Os}_3(\text{CO})_{10}(\text{h}^2\text{-C}_8\text{H}_{14})_2$ (C_8H_{14} = cyclooctene) to form a double edge-bridged cluster, $\text{Os}_3(\mu\text{-H})(\mu\text{-O}_2\text{CH})(\text{CO})_{10}$, with the formate ligand bridging through the oxygen atoms¹⁷.

The fragments of carbonic acid, in the form of CO_2 and H_2O , add to Rh complexes, such as $\text{HRh}(\text{PPr-}i_3)_3$, which, in THF at RT in 2h, yield¹⁸ 85% of the six-coordinated $\text{H}_2\text{Rh}(\text{O}_2\text{COH})(\text{PPr-}i_3)_2$.

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4. B. F. G. Johnson, J. Lewis, T. L. Odiaka, P. R. Raithby, *J. Organomet. Chem.*, **216**, C56 (1981).
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14. T. Yoshida, S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134 (1977).
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1.10.5.6.2. Involving Hydrogen-Sulfur Bonds.

The hydrogen-sulfur bonds of H_2S , RSH (R = alkyl, aryl) and RC(O)SH add to low-valent transition-metal complexes. Unsaturated Rh, Ir and Pt complexes add¹ H_2S . The complexes $\text{RhCl}(\text{PPh}_3)_3$, $\text{IrCl}(\text{CO})\text{PPh}_3$ and $\text{Pt}(\text{PPh}_3)_3$ in benzene at RT react with H_2S to form $\text{HRh}(\text{SH})\text{Cl}(\text{PPh}_3)_2$ (82%)², $\text{HIr}(\text{SH})\text{Cl}(\text{PPh}_3)_2$ (100%)² and $\text{HPt}(\text{SH})(\text{PPh}_3)_2$ (80%)³, respectively. Thiophenol also adds to the former complexes, giving high yields of the analogous oxidative-addition products^{2,3}.

The mixed thioether-thiol, $\text{HSCH}_2\text{CH}_2\text{SMe}$, when treated with $\text{Pt}(\text{PPh}_3)_3$ forms⁴ the hydride, $\text{HPt}(\text{SCH}_2\text{CH}_2\text{SMe})(\text{PPh}_3)_3$ in which both the thiolate and the thioether are coordinated to Pt. The compound $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SMe}$ transforms $\text{Pt}(\text{PPh}_3)_3$ to yield $\text{HPt}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SMe})(\text{PPh}_3)_3$, which has a four-coordinated, planar structure with the terminal thioether group uncoordinated.

When HSMc is bubbled through the binuclear complex, $[\text{HPt}_2(\text{CO})(\mu\text{-dppm})_2]\text{PF}_6$, in CH_2Cl_2 , a pale yellow precipitate of $[\text{H}_2\text{Pt}(\mu\text{-SMe})(\mu\text{-dppm})_2]\text{PF}_6$ is obtained in 72% yield⁵ [dppm = bis(diphenylphosphino)methane].

The cis-diazo Pt complex, $\text{Pt}(\text{N}_3)_2(\text{PPh}_3)_2$, reacts with HSC(O)Me to yield⁶ trans- $\text{HPt}[\text{SC(O)Me}](\text{PPh}_3)_2$. Thioacids also add to $\text{Pt}(\text{PPh}_3)_4$ to form $\text{HPt}[\text{SC(O)R}](\text{PPh}_3)_2$ (R = Me, Ph)⁷.

The cluster $\text{Ru}_3(\text{CO})_{12}$ can add EtSH or $n\text{-BuSH}$ oxidatively in C_6H_6 at reflux in 15 min to form $\text{HRu}_3(\text{SR})(\text{CO})_{10}$ in 72 or 50% yield, respectively⁸. The Os analogues

1.10. Formation of Bonds between Hydrogen and Transition Metals 203
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 1.10.5.6. of Hydrogen-Group VIB Element Bonds

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1.10.6. by Protonation

1.10.6.1. of Neutral and Cationic Complexes

1.10.6.1.1. Which Are Mononuclear: Scope.

Transition-metal complexes can serve as proton acceptors. Protonation, like the addition of covalent hydrogen—element bonds (§1.10.5), is a formal oxidative addition and so requires a formal d-electron configuration of d^2 or higher. The reaction is common for complexes of early as well as late transition metals¹⁻³. Table 1 lists examples for even d-electron configurations.

Protonation of d^0 complexes, such as $(\text{h}^5\text{-C}_3\text{H}_5)_2\text{TaH}_3$, does not give stable hydrides. For less-apparent reasons, protonation of some d^{10} complexes such as those of Au(I) and Hg(II) also does not give stable hydrides. Transient species, such as $[\text{Me}_2\text{HgH}]^+$, are observed in the gas phase²⁴, and hydride bridges to Au are known^{25,26}.

With many neutral complexes the protonated cation can be identified in acid [by observation of an upfield resonance in the ^1H nuclear magnetic resonance (NMR)] and, therefore, is frequently prepared in situ. However, isolation can be difficult because protonation generally is reversible. (In Table 1 no counterion is written when the cationic hydride is prepared only in solution; an anion is shown where a solid product is isolated.) For example, ferrocene is protonated⁵ in aq BF_3 , but isolation is difficult and is accomplished only for HCl and AlCl_3 in CH_2Cl_2 (giving the $[\text{AlCl}_4]^-$ salt²⁷) and for HX and BX_3 in benzene (giving the $[\text{BX}_4]^-$ salts⁹). Oxidation to the ferricenium cation and loss of HX to give ferrocenyldihaloboranes are complications.

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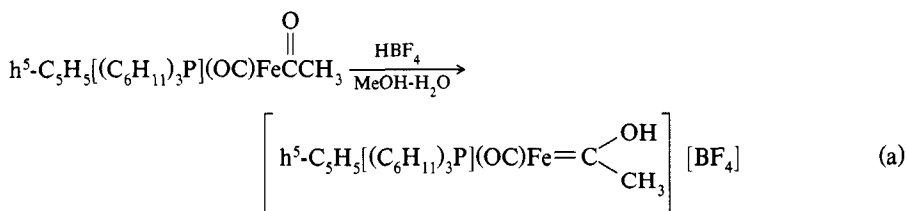
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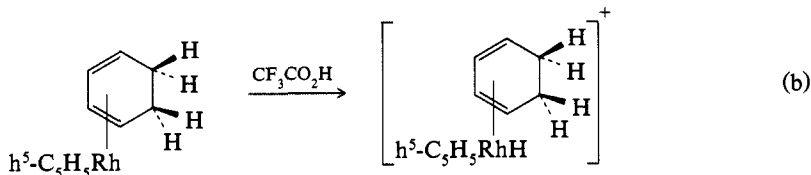
TABLE 1. FORMATION OF CATIONIC HYDRIDES BY PROTONATION
 OF NEUTRAL TRANSITION-METAL COMPLEXES

Neutral complex (d-electron configuration)	Acid	Cationic hydride (d-electron configuration)	Refs.
$(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2$ (d^2)	aq HCl	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_3]\text{Cl}$ (d^0)	4
$(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}$ (d^4)	aq HCl	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}_2]\text{Cl}$ (d^2)	5
$\eta^5\text{-C}_5\text{H}_5\text{Nb}(\text{CO})_4$ (d^4)	$\text{CF}_3\text{CO}_2\text{H}-\text{CH}_2\text{Cl}_2$	$[\eta^5\text{-C}_5\text{H}_5\text{Nb}(\text{CO})_4\text{H}]^+$ (d^2)	6
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ (d^6)	$\text{BX}_3\text{-HX}-\text{C}_6\text{H}_6$	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{FeH}][\text{BX}_4]$ (d^4)	7-9
$\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{PPh}_3$ (d^6)	$\text{CF}_3\text{CO}_2\text{H}-\text{CHCl}_3$	$[\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2(\text{PPh}_3)\text{H}]^+$ (d^4)	6, 10
$\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPhMe}_2$ (d^6)	$\text{CF}_3\text{SO}_3\text{H}-\text{CD}_2\text{Cl}_2$	$[\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{PPhMe}_2)\text{H}]^+$ (d^4)	11, 12
$\eta^6\text{-C}_6\text{H}_5\text{Me}_3\text{Cr}(\text{CO})_3$ (d^6)	$\text{FSO}_3\text{H}-\text{SO}_2$	$[\eta^6\text{-C}_6\text{H}_5\text{Me}_3\text{Cr}(\text{CO})_3\text{H}]^+$ (d^4)	12-16
$\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ (d^8)	HClO_4 (or HPF_6 or HBF_4) in EtOH	$[\text{Os}(\text{CO})_3(\text{PPh}_3)_2\text{H}][\text{ClO}_4]$ (d^6)	17
$\eta^5\text{-C}_5\text{Me}_5\text{Ir}(\text{CO})_2$ (d^8)	$\text{HBF}_4\text{-ether}$	$[\eta^5\text{-C}_5\text{Me}_5\text{Ir}(\text{CO})_2\text{H}][\text{BF}_4]$ (d^6)	18
$\eta^5\text{-C}_5\text{Me}_5\text{Co}(\text{PMe}_3)_2$ (d^8)	$\text{MeOH}-\text{NH}_4\text{PF}_6$	$[\eta^5\text{-C}_5\text{Me}_5\text{Co}(\text{PMe}_3)_2\text{H}][\text{PF}_6]$ (d^6)	19
$\text{Fe}[\text{P}(\text{OMe})_3]_3$ (d^8)	$\text{NH}_4\text{PF}_6\text{-THF}$	$[\text{HFe}[\text{P}(\text{OMe})_3]_3]^+$ (d^6)	20
$\text{Pt}(\text{PPh}_3)_3$ (d^{10})	$\text{CF}_3\text{CO}_2\text{H}$	$[\text{Pt}(\text{PPh}_3)_3\text{H}][(\text{CF}_3\text{CO}_2)_2\text{H}]$ (d^8)	21, 22
$\text{Pd}(\text{PEt}_3)_4$ (d^{10})	$\text{EtOH}-\text{NaBPh}_4\text{-HCl}$	$[\text{Pd}(\text{PEt}_3)_3\text{H}][\text{BPh}_4]$ (d^8)	23

Competition for protons between the metal and the ligand is common; e.g., dienes and other unsaturated ligands undergo protonation, as do electronegative ligand atoms, such as acyl oxygens²⁸:



Protonation at the latter is favored kinetically because it can occur with little electronic rearrangement. Initial protonation at the metal may give a cation in which the hydride is exchanged between the metal and various ligand sites; e.g., protonation of $\eta^5\text{-C}_5\text{H}_5\text{Rh}(1,3\text{-cyclohexadiene})$ gives a hydride cation (which can be isolated as a $[\text{PF}_6]^-$ salt):

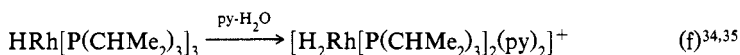
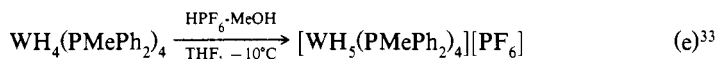
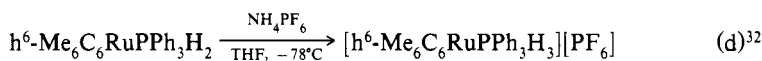
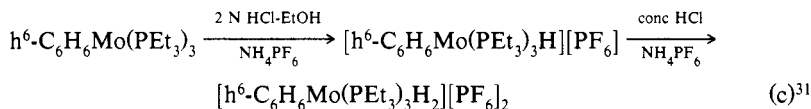


When $\text{CF}_3\text{CO}_2\text{D}$ is used as the acid proton, nuclear magnetic resonance (NMR) shows rapid and stereospecific exchange between the Rh hydride and the two endo positions on the six-membered ring, reflecting the reversible transfer of the Rh hydride to endo sites at the ends of the diene system²⁹.

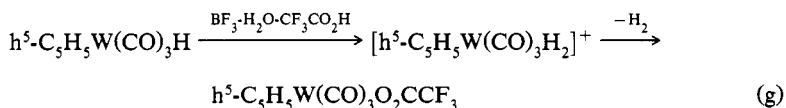
Protonation of organometallic complexes containing metal-carbon σ bonds leads to cleavage of those bonds—a reaction assumed to proceed by formation of a cationic

hydride followed by C—H elimination. However, protonation by strong acids of $\text{CH}_3\text{Mn}(\text{CO})_5$ in the gas phase gives an observable cation (by protonation at the metal to form $[\text{CH}_3\text{Mn}(\text{CO})_5\text{H}]^+$), whereas weak acids give immediate methane loss without intermediate formation of the cation³⁰. Protic cleavage of a metal—carbon σ bond may occur without formation of a M—H bond, presumably by direct electrophilic attack on the electron pair in the σ bond.

Although stable cationic polyhydrides are formed on protonation of some hydrides, e.g., the first two entries in Table 1 and:



many cationic dihydrides are unstable to H_2 evolution. The protonation of $\text{h}^5\text{-C}_5\text{H}_5\text{-W}(\text{CO})_3\text{H}$ gives a cationic dihydride¹³ that evolves H_2 within several hours at RT:



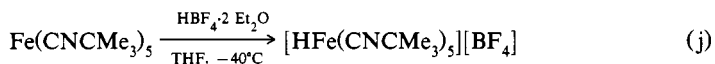
The protonation of $\text{HCo}[\text{P}(\text{OCHMe}_2)_3]_4$ gives a cationic dihydride that evolves³⁹ H_2 within 1 day at 20°C :



Care must be taken in protonations to avoid further protonation and H_2 evolution; e.g., although clean monoprotection of $\text{Fe}[\text{P}(\text{OMe})_3]_5$ can be effected by NH_4PF_6 (see Table 1), $\text{CH}_3\text{CO}_2\text{H}$ decomposes the cationic hydride initially formed^{20,40}:



Careful protonation of $\text{Fe}(\text{CNCMe}_3)_5$ at -40°C allows the isolation of $[\text{HFe}(\text{CNCMe}_3)_5]^+$:

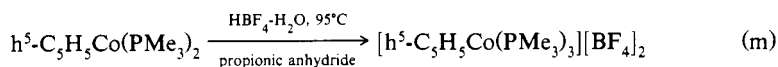
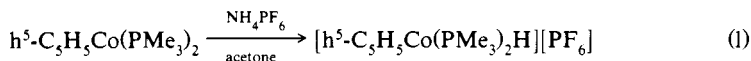


but protonation with xs acid at RT gives loss of H_2 and formation of a dication⁴¹:



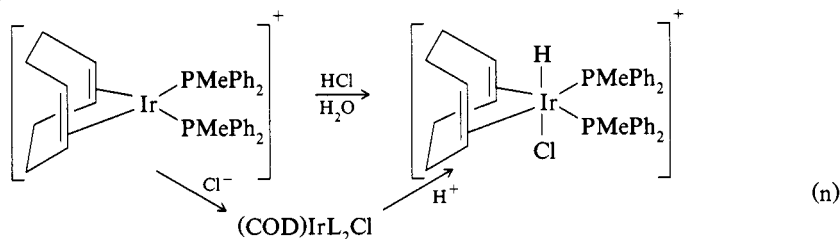
If the addition of aq HBF_4 to $\text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ is not carefully controlled, the heat from hydrolysis of the propionic anhydride solvent causes H_2 evolution and formation

of a dication⁴²:



Although $\text{Pt(PPh}_3)_4$ becomes $[\text{Pt(PPh}_3)_3\text{H}]^+$ between $\text{pH} = 2$ and an acidity function, $\text{H}_0 \approx -10$, it reacts³⁸ and generates H_2 at $\text{H}_0 < -10$. Protic cleavage of hydride ligands may occur by direct electrophilic attack on the electron pair in the existing M-H σ bond without the formation of a new M-H σ bond (in analogy with the process discussed above for cleavage of M-C σ bonds).

Cationic complexes can be protonated, e.g., in Eq. (c), and in §1.10.6.1.2, where the equilibrium constant for protonation is discussed. However, in:



where $\text{L} = \text{PMe}_2\text{Ph}$, both kinetic evidence⁴¹ and isolation of the intermediate shown⁴² establish that the anion, X^- , of a coordinating acid must be added, forming a neutral intermediate, before protonation can occur. It seems likely that this pattern will prove common for cationic complexes.

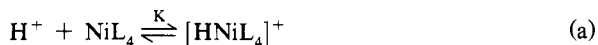
(J. R. NORTON)

1. J. C. Kotz, D. G. Pedrotty, *Organomet. Chem. Rev., A*, 4, 479 (1969).
2. D. F. Shriver, *Acc. Chem. Res.*, 3, 231 (1970).
3. R. A. Schunn, in *Transition-Metal Hydrides*, E. L. Muetterties, ed., Marcel Dekker, New York, 1971, p. 203.
4. M. L. H. Green, J. A. McCleverty, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).
5. M. L. H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).
6. B. V. Lokshin, A. A. Pasinsky, N. E. Kolobova, K. N. Anisimov, T. V. Makarov, *J. Organomet. Chem.*, 55, 315 (1973).
7. T. J. Curphey, J. O. Santer, M. Rosenblum, J. H. Richards, *J. Am. Chem. Soc.*, 82, 5249 (1960).
8. T. E. Bitterwolf, A. C. Ling, *J. Organomet. Chem.*, 40, 197 (1972).
9. W. Siebert, W. Ruf, K.-J. Schaper, T. Renk, *J. Organomet. Chem.*, 128, 219 (1977).
10. G. A. Panosyan, P. V. Petrovskii, N. I. Pyshnograveya, N. E. Kolobova, V. N. Setkina, E. I. Fedin, *J. Organomet. Chem.*, 108, 209 (1976).
11. B. V. Lokshin, A. G. Ginzburg, V. N. Setkina, D. N. Kursanov, I. B. Nemirovskaya, *J. Organomet. Chem.*, 37, 347 (1972).
12. T. C. Flood, E. Rosenberg, A. Sarhangi, *J. Am. Chem. Soc.*, 99, 4334 (1977).
13. A. Davison, W. McFarlane, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).
14. D. N. Kursanov, V. N. Setkina, P. V. Petrovskii, V. I. Zdanovich, N. K. Baranetskaya, I. D. Rubin, *J. Organomet. Chem.*, 37, 339 (1972).
15. G. A. Olah, S. H. Yu, *J. Org. Chem.*, 41, 717 (1976).
16. C. P. Lilly, R. A. Sahatjian, *Inorg. Chem.*, 11, 889 (1972).
17. K. R. Laing, W. R. Roper, *J. Chem. Soc., A*, 1889 (1969).
18. J. Plank, D. Riedel, W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 19, 937 (1980).
19. H. Werner, B. Heiser, B. Klingert, R. Döfel, *J. Organomet. Chem.*, 240, 179 (1982).
20. T. V. Harris, J. W. Rathke, E. L. Muetterties, *J. Am. Chem. Soc.*, 100, 6966 (1978).
21. F. Cariati, R. Ugo, F. Bonati, *Inorg. Chem.*, 5, 1128 (1966).

22. D. M. Roundhill, in *Transition-Metal Hydrides*, R. Bau, ed., Advances in Chemistry Series No. 167, American Chemical Society, Washington, DC, 1978, p. 160.
23. R. A. Schunn, *Inorg. Chem.*, **15**, 208 (1976).
24. J. A. Stone, J. R. M. Camicioli, M. C. Baird, *Inorg. Chem.*, **19**, 3128 (1980).
25. H. Lehner, D. Matt, P. S. Pregosin, L. M. Venanzi, A. Albinati, *J. Am. Chem. Soc.*, **104**, 6825 (1982).
26. M. Green, A. G. Orpen, I. D. Salter, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 813 (1982).
27. M. Rosenblum, J. O. Santer, W. G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963).
28. M. L. H. Green, L. C. Mitchard, M. G. Swanwick, *J. Chem. Soc., A*, 794 (1971).
29. B. F. G. Johnson, J. Lewis, D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 2084 (1972).
30. A. E. Stevens, J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 245 (1979).
31. M. L. H. Green, L. C. Mitchard, W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1361 (1974).
32. H. Werner, H. Kletzin, *J. Organomet. Chem.*, **243**, C59 (1983).
33. E. Carmona-Guzman, G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1716 (1977).
34. T. Yoshida, T. Okano, Y. Ueda, S. Otsuka, *J. Am. Chem. Soc.*, **103**, 3411 (1981).
35. R. F. Jones, D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 58 (1981).
36. E. L. Muetterties, P. L. Watson, *J. Am. Chem. Soc.*, **100**, 6978 (1978).
37. E. L. Muetterties, J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974).
38. J.-M. Bassett, L. J. Ferugia, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1789 (1980).
39. H. Werner, W. Hofmann, *Chem. Ber.*, **110**, 3481 (1977).
40. P. Foley, G. M. Whitesides, *Inorg. Chem.*, **19**, 1402 (1980).
41. V. Ashworth, J. E. Singleton, D. J. A. de Waal, E. Singleton, E. van der Stok, *J. Chem. Soc., Dalton Trans.*, 340 (1978).
42. R. H. Crabtree, J. M. Quirk, T. Fillebeen-Khan, G. E. Morris, *J. Organomet. Chem.*, **181**, 203 (1979).

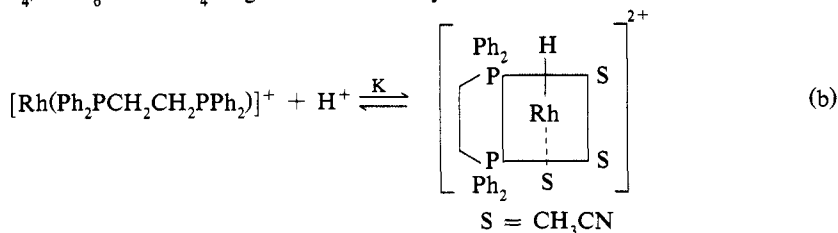
1.10.6.1.2. Which Are Mononuclear: Position of the Protonation Equilibria.

Few quantitative data are available. The pK_a of $[(h^5-C_5H_5)_2ReH_2]^+$ in 60% aq dioxane is¹ 8.5. The equilibrium constants for protonation of NiL_4 by H_2SO_4 in MeOH at 0°C:



are known for phosphite ligands and for $L_2 = Ph_2PCH_2CH_2PPh_2$. Values of K range from 410 M^{-1} for $Ni(Ph_2PCH_2CH_2PPh_2)_2$ to 34 M^{-1} for $Ni[P(OR)_3]_4$ ($R = \text{Me}$, or Et) to small values for phosphites with electron-withdrawing substituents². Under the same conditions the equilibrium constant for protonation of $Ni(CO)_4$ is only² 10^{-7} M^{-1} . In acetonitrile, $Ni[P(OEt)_3]_4$ is fully protonated by 1 equiv of $HClO_4$ or H_2SO_4 and completely unprotonated by CH_3CO_2H ; $[Ni(P(OEt)_3)_4H]^+$ has the acid strength³ of trifluoroacetic acid in CH_3CN . In the same solvent the pK_a values⁴ of $[M[P(OMe)_3]_4H]^+$ are 18.5, 8.0 and 12.3 for $M = \text{Pt}$, Pd and Ni , respectively; in MeOH they are 10.2, 1.0 and 1.5.

In MeOH or in acetonitrile the d^8 cation $[Rh(Ph_2PCH_2CH_2PPh_2)]^+$ is protonated by HBF_4 , HPF_6 or $HClO_4$ to give a dicationic hydride:



The equilibrium constant in MeOH is⁵ 11 M^{-1} . For $IrCl(CO)(AsPh_3)_2$ in MeOH at

208 1.10. Formation of Bonds between Hydrogen and Transition Metals
 1.10.6. by Protonation
 1.10.6.1. of Neutral and Cationic Complexes

22. D. M. Roundhill, in *Transition-Metal Hydrides*, R. Bau, ed., Advances in Chemistry Series No. 167, American Chemical Society, Washington, DC, 1978, p. 160.
23. R. A. Schunn, *Inorg. Chem.*, **15**, 208 (1976).
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33. E. Carmona-Guzman, G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1716 (1977).
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1.10.6.1.2. Which Are Mononuclear:

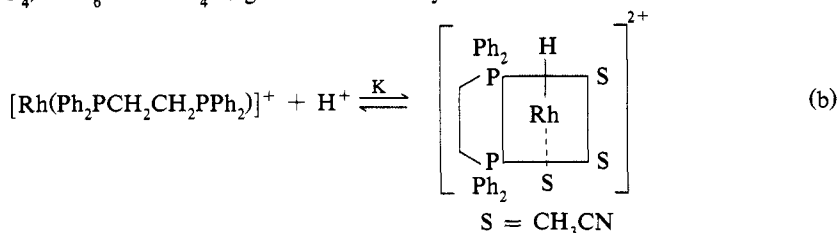
Position of the Protonation Equilibria.

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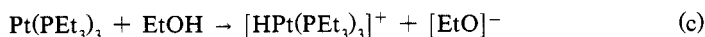


The equilibrium constant in MeOH is⁵ 11 M^{-1} . For $IrCl(CO)(AsPh_3)_2$ in MeOH at

RT, the protonation equilibrium constant is 203 M^{-1} ; for $\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$ it is 75 M^{-1} . Similar K values are found for Ir and Rh complexes with phosphine and halide ligands.⁶ Finally, ruthenocene is half-protonated in H_2SO_4 with an acidity function, H_0 , of -5.7 , whereas half-protonation of ferrocene requires⁷ an H_0 of -7.7 .

From qualitative knowledge about protonation equilibria, basicity tends to increase down a periodic column: ruthenocene (see above) is protonated in less acidic media than is ferrocene⁷, $\text{cis-OsH}_2(\text{PMe}_3)_4$ is protonated in less acidic media than is its Fe analogue⁸, $\text{h}^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{PPh}_3$ is protonated in less acidic media than is⁹ $\text{h}^5\text{-C}_5\text{H}_5\text{-Mn}(\text{CO})_2\text{PPh}_3$ and $\text{h}^5\text{-C}_5\text{H}_5\text{Nb}(\text{CO})_3\text{PPh}_3$ is protonated in less acidic media than is⁹ $\text{h}^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{PPh}_3$. However, the quantitative data above show that basicity decreases from Ni to Pd for $\text{M}[\text{P}(\text{OMe})_3]_4$. The replacement of π -acceptor by σ -donor ligands also increases basicity: $\text{h}^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{PPh}_3$ requires less acidic media for protonation than does¹⁰ $\text{h}^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$, and base strength increases in the order¹¹ $\text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2 < \text{h}^5\text{-C}_5\text{H}_5\text{Co}[\text{P}(\text{OR})_3]_2 < \text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$.

The presence of sufficiently powerful σ -donor ligands can make a metal a proton acceptor. The trialkylphosphine ligands in¹² $\text{Pt}(\text{PEt}_3)_3$, and¹³ $\text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ make the metals sufficiently basic to deprotonate EtOH and H_2O :



and $\text{Ni}(\text{PEt}_3)_4$, $\text{Pd}(\text{PEt}_3)_3$ and $\text{Pd}(\text{PEt}_3)_4$ also form hydride cations by deprotonating¹⁴ EtOH .

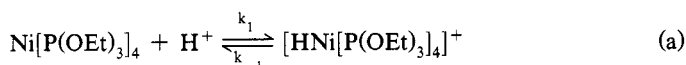
Tricarbonyl complexes are more basic than their dinitrosyl analogues¹⁵; e.g., $[\text{HMoL}(\text{CO})_3][\text{BF}_4]$ ($\text{L} = 1,4,7\text{-triazacyclononane}$) is a strong aqueous acid, whereas $[\text{HMoL}(\text{NO})_2][\text{ClO}_4]$ is weak¹⁶.

(J. R. NORTON)

1. M. L. H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).
2. C. A. Tolman, *Inorg. Chem.*, **11**, 3128 (1972).
3. C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 4217 (1970).
4. R. G. Pearson, personal communication, 1985.
5. J. Halpern, D. P. Riley, A. S. C. Chan, J. J. Pluth, *J. Am. Chem. Soc.*, **99**, 8055 (1977).
6. R. G. Pearson, C. T. Kresge, *Inorg. Chem.*, **20**, 1878 (1981).
7. G. Cerichelli, G. Illuminati, G. Ortaggi, A. M. Giuliani, *J. Organomet. Chem.*, **127**, 357 (1977).
8. H. Werner, J. Gotzig, *Organometallics*, **2**, 547 (1983).
9. B. V. Lokshin, A. A. Pasinsky, N. E. Kolobova, K. N. Anisimov, Y. V. Makarov, *J. Organomet. Chem.*, **55**, 315 (1973).
10. D. N. Kursanov, V. N. Setkina, P. V. Petrovskii, V. I. Zdanovich, N. K. Baranetskaya, I. D. Rubin, *J. Organomet. Chem.*, **37**, 339 (1972).
11. H. Werner, *Pure Appl. Chem.*, **54**, 177 (1982).
12. D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 3543 (1971).
13. H. Werner, W. Hofmann, *Angew. Chem., Int. Ed. Engl.*, **17**, 464 (1978).
14. R. A. Schunn, *Inorg. Chem.*, **15**, 208 (1976).
15. B. E. Bursten, M. G. Gatter, *J. Am. Chem. Soc.*, **106**, 2554 (1984).
16. P. Chaudhuri, K. Wieghart, Y.-H. Tsai, C. Krüger, *Inorg. Chem.*, **23**, 427 (1984).

1.10.6.1.3. Which Are Mononuclear: Rates.

Even fewer quantitative data are available on protonation rates than on equilibria. For the protonation¹:



1.10. Formation of Bonds between Hydrogen and Transition Metals 209

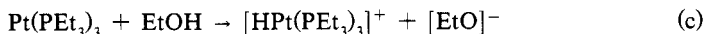
1.10.6. by Protonation

1.10.6.1. of Neutral and Cationic Complexes

RT, the protonation equilibrium constant is 203 M^{-1} ; for $\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$ it is 75 M^{-1} . Similar K values are found for Ir and Rh complexes with phosphine and halide ligands.⁶ Finally, ruthenocene is half-protonated in H_2SO_4 with an acidity function, H_0 , of -5.7 , whereas half-protonation of ferrocene requires⁷ an H_0 of -7.7 .

From qualitative knowledge about protonation equilibria, basicity tends to increase down a periodic column: ruthenocene (see above) is protonated in less acidic media than is ferrocene⁷, $\text{cis-OsH}_2(\text{PMe}_3)_4$ is protonated in less acidic media than is its Fe analogue⁸, $\text{h}^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2\text{PPh}_3$ is protonated in less acidic media than is⁹ $\text{h}^5\text{-C}_5\text{H}_5\text{-Mn}(\text{CO})_2\text{PPh}_3$ and $\text{h}^5\text{-C}_5\text{H}_5\text{Nb}(\text{CO})_3\text{PPh}_3$ is protonated in less acidic media than is⁹ $\text{h}^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{PPh}_3$. However, the quantitative data above show that basicity decreases from Ni to Pd for $\text{M}[\text{P}(\text{OMe})_3]_4$. The replacement of π -acceptor by σ -donor ligands also increases basicity: $\text{h}^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{PPh}_3$ requires less acidic media for protonation than does¹⁰ $\text{h}^6\text{-C}_6\text{H}_6\text{Cr}(\text{CO})_3$, and base strength increases in the order¹¹ $\text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2 < \text{h}^5\text{-C}_5\text{H}_5\text{Co}[\text{P}(\text{OR})_3]_2 < \text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$.

The presence of sufficiently powerful σ -donor ligands can make a metal a proton acceptor. The trialkylphosphine ligands in¹² $\text{Pt}(\text{PEt}_3)_3$, and¹³ $\text{h}^5\text{-C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ make the metals sufficiently basic to deprotonate EtOH and H_2O :



and $\text{Ni}(\text{PEt}_3)_4$, $\text{Pd}(\text{PEt}_3)_3$ and $\text{Pd}(\text{PEt}_3)_4$ also form hydride cations by deprotonating¹⁴ EtOH .

Tricarbonyl complexes are more basic than their dinitrosyl analogues¹⁵; e.g., $[\text{HMoL}(\text{CO})_3][\text{BF}_4]$ ($\text{L} = 1,4,7\text{-triazacyclononane}$) is a strong aqueous acid, whereas $[\text{HMoL}(\text{NO})_2][\text{ClO}_4]$ is weak¹⁶.

(J. R. NORTON)

1. M. L. H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).
2. C. A. Tolman, *Inorg. Chem.*, 11, 3128 (1972).
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4. R. G. Pearson, personal communication, 1985.
5. J. Halpern, D. P. Riley, A. S. C. Chan, J. J. Pluth, *J. Am. Chem. Soc.*, 99, 8055 (1977).
6. R. G. Pearson, C. T. Kresge, *Inorg. Chem.*, 20, 1878 (1981).
7. G. Cerichelli, G. Illuminati, G. Ortaggi, A. M. Giuliani, *J. Organomet. Chem.*, 127, 357 (1977).
8. H. Werner, J. Gotzig, *Organometallics*, 2, 547 (1983).
9. B. V. Lokshin, A. A. Pasinsky, N. E. Kolobova, K. N. Anisimov, Y. V. Makarov, *J. Organomet. Chem.*, 55, 315 (1973).
10. D. N. Kursanov, V. N. Setkina, P. V. Petrovskii, V. I. Zdanovich, N. K. Baranetskaya, I. D. Rubin, *J. Organomet. Chem.*, 37, 339 (1972).
11. H. Werner, *Pure Appl. Chem.*, 54, 177 (1982).
12. D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, E. L. Muetterties, *J. Am. Chem. Soc.*, 93, 3543 (1971).
13. H. Werner, W. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 17, 464 (1978).
14. R. A. Schunn, *Inorg. Chem.*, 15, 208 (1976).
15. B. E. Bursten, M. G. Gatter, *J. Am. Chem. Soc.*, 106, 2554 (1984).
16. P. Chaudhuri, K. Wieghart, Y.-H. Tsai, C. Krüger, *Inorg. Chem.*, 23, 427 (1984).

1.10.6.1.3. Which Are Mononuclear: Rates.

Even fewer quantitative data are available on protonation rates than on equilibria. For the protonation¹:



at 25°C in MeOH, $k_1 = 1550 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1} = 45 \text{ s}^{-1}$.

The rate of protonation of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in MeOH reflects the rate of prior solvent coordination².

The rate constants for protonation at the metal of (6-dimethylamino-fulvene) $\text{M}(\text{CO})_3$ increase³ in the order $\text{Cr} < \text{Mo} < \text{W}$; quantitative results are given³, but they appear unreliable. Proton transfer between protonated and unprotonated forms of (arene) $\text{Cr}(\text{CO})_3$ is fast on the NMR time scale and occurs by rate-determining proton removal by the conjugate base ($[\text{FSO}_3]^-$) of the acid employed⁴ (FSO_3H).

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1.10.6.1.4. Which Are Polynuclear.

Polynuclear complexes are frequently protonated in strong acid. In Table 1 the anion is shown when the hydride cation is isolated; if it is omitted, the hydride cation is made only in situ. Often the location (terminal or bridging and, if the latter, among which metal atoms) of the hydrogen atom is not known, although an upfield shift in the ^1H NMR identifies the hydrogen as attached to the metal framework.

Substituent effects on protonation equilibria are similar to those for mononuclear compounds. The metal-metal-bonded dimers, $[(\mu\text{-SCH}_3)\text{Fe}(\text{CO})_2\text{L}]_2$, are stronger proton bases¹² when L is a strong donor phosphine such as PMe_3 , than when L is PPh_3 . The pK_b of $[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ in acetic acid is 7.5; both the phosphite-substituted dimer $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$ and the second-row analogue, $[\text{h}^5\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2]_2$, are stronger proton bases⁴. Proton-transfer rates involving $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$ and its protonated analogue are faster than those involving the $[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ system and its Ru analogue⁴, and $\text{Os}_3(\text{CO})_{12}$ is ca. five times more basic¹³ than $\text{Ru}_3(\text{CO})_{12}$.

As is seen in Table 1, protonation occurs on the metal-metal-bonded framework despite the presence of hydride, sulfur ligands, or organic fragments. Diprotonation may result in protonation of a carbon ligand, but only after initial protonation on the metal core; e.g., $\text{HRu}_3(\text{CO})_9\text{C}\equiv\text{CCMe}_3$ undergoes monoprotection on a Ru—Ru bond in $\text{CF}_3\text{CO}_2\text{H}$; in HSO_3Cl or H_2SO_4 a dication is formed, with the second proton going onto carbon¹⁴.

TABLE 1. CATIONIC HYDRIDES RESULTING FROM THE PROTONATION OF POLYNUCLEAR COMPLEXES

Polynuclear complex	Acid	Cationic hydride	Refs.
$[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$	HF-PCl_5	$[[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{H}][\text{PF}_6]$	1
$\text{Re}(\text{CO})_5(\mu\text{-Ar}_2\text{PC}_6\text{H}_4)_2$	$\text{CF}_3\text{SO}_3\text{H-CD}_2\text{Cl}_2$	$[\text{Re}(\text{CO})_5(\mu\text{-Ar}_2\text{PC}_6\text{H}_4)(\mu\text{-H})]_2$	2
$\text{Mo}(\text{CO})_3^a$		$\text{Mo}(\text{CO})_3^+ a$	
$[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	HCl-PF_5	$[[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{H}][\text{PF}_6]$	3, 4
$\text{Os}_3(\text{CO})_{12}$	$\text{H}_2\text{SO}_4\text{-NH}_4\text{PF}_6$	$[\text{HOs}_3(\text{CO})_{12}][\text{PF}_6]$	5, 6
$\text{H}_2\text{Os}_3(\text{CO})_9\text{C}\equiv\text{CH}_2$	$\text{CF}_3\text{CO}_2\text{H-CDCl}_3$	$[\text{H}_2\text{Os}_3(\text{CO})_9\text{C}\equiv\text{CH}_2]^+$	7
$\text{HOs}_3(\text{CO})_9(\text{PEt}_3)\text{SPh}$	$\text{H}_2\text{SO}_4\text{-NH}_4\text{PF}_6$	$[\text{H}_2\text{Os}_3(\text{CO})_9(\text{PEt}_3)\text{SPh}][\text{PF}_6]$	8
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$	$\text{HBF}_4\text{-H}_2\text{O-Et}_2\text{O}$	$[(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3\text{H}][\text{BF}_4]$	9
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{CoPMe}_2$	$\text{CF}_3\text{CO}_2\text{H-NH}_4\text{PF}_6$	$[(\text{h}^5\text{-C}_5\text{H}_5)_2\text{CoPMe}_2\text{H}][\text{PF}_6]$	10
$(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pt}_2\text{Cl}_2$	$\text{HCl-CHCl}_3\text{-NH}_4\text{PF}_6\text{-MeOH}$	$[(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pt}_2\text{Cl}_2\text{H}][\text{PF}_6]$	11

^a Ar = p-tolyl.

210 1.10. Formation of Bonds between Hydrogen and Transition Metals

1.10.6. by Protonation

1.10.6.1. of Neutral and Cationic Complexes

at 25°C in MeOH, $k_1 = 1550 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1} = 45 \text{ s}^{-1}$.

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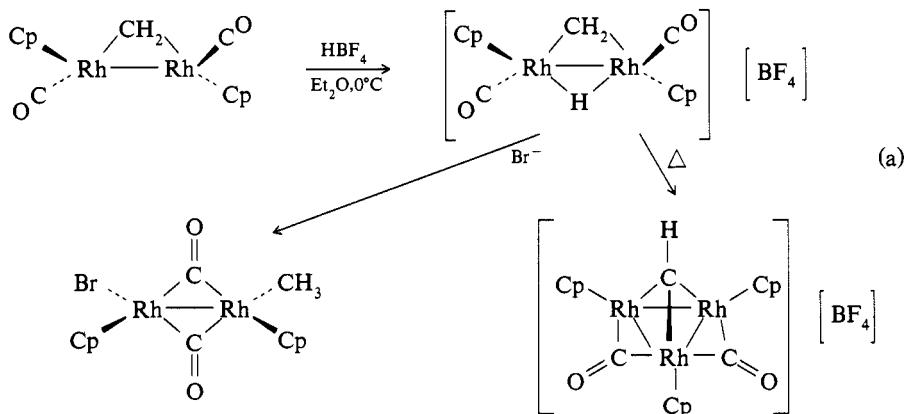
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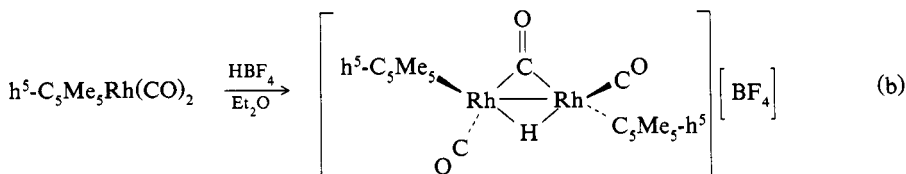
Polynuclear complex	Acid	Cationic hydride	Refs.
$[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2$	HF-PCl_5	$[[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]_2\text{H}][\text{PF}_6]$	1
$\text{Re}(\text{CO})_4(\mu\text{-Ar}_2\text{PC}_6\text{H}_4)_2$	$\text{CF}_3\text{SO}_3\text{H-CD}_2\text{Cl}_2$	$[\text{Re}(\text{CO})_4(\mu\text{-Ar}_2\text{PC}_6\text{H}_4)(\mu\text{-H})\text{Mo}(\text{CO})_3]^{+a}$	2
$[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	HCl-PF_5	$[[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{H}][\text{PF}_6]$	3, 4
$\text{Os}_3(\text{CO})_{12}$	$\text{H}_2\text{SO}_4\text{-NH}_4\text{PF}_6$	$[\text{HOs}_3(\text{CO})_{12}][\text{PF}_6]$	5, 6
$\text{H}_2\text{Os}_3(\text{CO})_9\text{C}\equiv\text{CH}_2$	$\text{CF}_3\text{CO}_2\text{H-CDCl}_3$	$[\text{H}_2\text{Os}_3(\text{CO})_9\text{C}\equiv\text{CH}_2]^{+}$	7
$\text{HOs}_3(\text{CO})_9(\text{PEt}_3)\text{SPh}$	$\text{H}_2\text{SO}_4\text{-NH}_4\text{PF}_6$	$[\text{H}_2\text{Os}_3(\text{CO})_9(\text{PEt}_3)\text{SPh}][\text{PF}_6]$	8
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$	$\text{HBF}_4\text{-H}_2\text{O-Et}_2\text{O}$	$[(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3\text{H}][\text{BF}_4]$	9
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{CoPMe}_2$	$\text{CF}_3\text{CO}_2\text{H-NH}_4\text{PF}_6$	$[(\text{h}^5\text{-C}_5\text{H}_5)_2\text{CoPMe}_2\text{H}][\text{PF}_6]$	10
$(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pt}_2\text{Cl}_2$	$\text{HCl-CHCl}_3\text{-NH}_4\text{PF}_6\text{-MeOH}$	$[(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pt}_2\text{Cl}_2\text{H}][\text{PF}_6]$	11

^a Ar = p-tolyl.

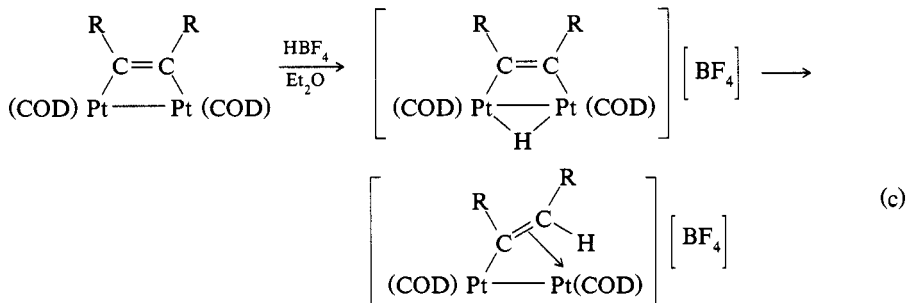
Preferential protonation of an organic ligand rather than a metal-metal bond occurs when the latter is sterically inaccessible, as for $\text{Ru}_2(\mu\text{-CH}_2)_3(\text{PMe}_3)_6$ where the Ru-Ru bond is already triply bridged¹⁵. In contrast, protonation of $\mu\text{-CH}_2[\text{h}^5\text{-C}_5\text{H}_5\text{-Rh(CO)}]_2$ occurs at the metal-metal bond, although deuterium labeling shows rapid exchange of the hydride and methylene protons and suggests that the methyl tautomer of the observed structure is accessible. Addition of a coordinating anion allows isolation of a dimer with a methyl ligand⁹. Protonation labilizes the Rh-Rh bond and leads to the formation of a $\mu_3\text{-CH}$ trimer:



just as protonation of a $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3$ (as in Table 1) leads to formation⁹ of a $\mu\text{-CH}_3$ trimer. The reverse process is also possible: protonation of a mononuclear complex can form a protonated metal-metal bond¹⁶:



Protonation of a metal-metal bond may be favored kinetically even when it is disfavored thermodynamically. The diplatinacyclobutene shown initially forms an isolable bridged cationic hydride which rearranges to a bridged vinyl complex¹⁷ on standing for 1 h at RT:



where $\text{R} = 4\text{-MeOC}_6\text{F}_4$.

(J. R. NORTON)

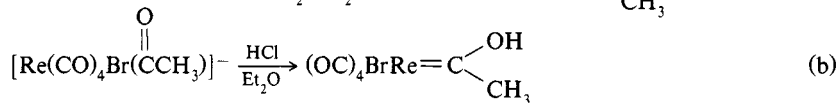
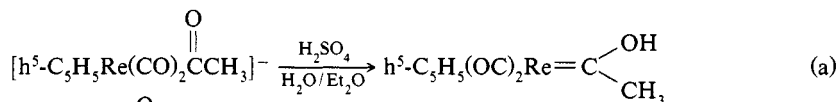
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3. D. A. Symon, T. C. Waddington, *J. Chem. Soc., A*, 953 (1971).
4. D. C. Harris, H. B. Gray, *Inorg. Chem.*, 14, 1215 (1975).
5. J. Knight, M. J. Mays, *J. Chem. Soc., A*, 711 (1970).
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7. A. J. Deeming, S. Hasso, M. Underhill, A. J. Canty, B. F. G. Johnson, W. G. Jackson, J. Lewis, T. W. Matheson, *J. Chem. Soc., Chem. Commun.*, 807 (1974).
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13. B. Delley, M. C. Manning, D. E. Ellis, J. Berkowitz, W. C. Troglor, *Inorg. Chem.*, 21, 2247 (1982).
14. C. Barner-Thorsen, E. Rosenberg, G. Saatjian, S. Aime, L. Milone, D. Osella, *Inorg. Chem.*, 20, 1592 (1981).
15. M. B. Hursthouse, R. A. Jones, K. M. Abdul Malik, G. Wilkinson, *J. Am. Chem. Soc.*, 101, 4128 (1979).
16. J. Plank, D. Riedel, W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 19, 937 (1980).
17. N. M. Boag, M. Green, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1281 (1980).

1.10.6.2. of Metal Anions

1.10.6.2.1. Which are Mononuclear: Scope.

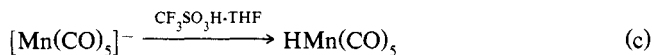
This widely used method is, just like the protonation of neutral complexes, a formal oxidative addition requiring a d-electron configuration between d^2 and d^{10} . In practice, most applications are to d-electron configurations between d^6 and d^{10} (see Table 1).

Most transition-metal anions give hydrides by protonation at the metal, but acyl anions generally give hydroxycarbene complexes instead of acyl hydrides¹⁸⁻²¹:



Because the charge on the acyl anion is localized at the acyl oxygen, protonation at that oxygen can occur with little electronic rearrangement, and O-protonation is favored kinetically. It is not clear whether hydroxycarbene complexes are more stable than acyl hydrides²².

Just as further protonation of a cationic hydride can lead to H_2 evolution and formation of a dication, further protonation of a neutral hydride can lead to H_2 loss and formation of a monocation. Although CF_3SO_3H in THF gives²³ $HMn(CO)_5$ from $[Mn(CO)_5]^-$:



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1.10.6. by Protonation

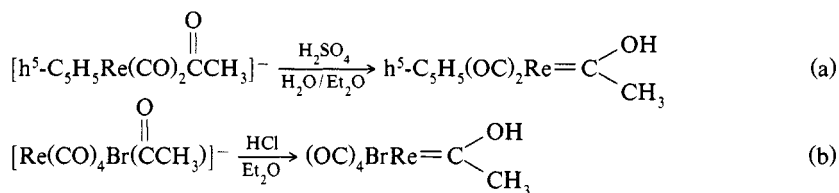
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14. C. Barner-Thorsen, E. Rosenberg, G. Saatjian, S. Aime, L. Milone, D. Osella, *Inorg. Chem.*, **20**, 1592 (1981).
15. M. B. Hursthouse, R. A. Jones, K. M. Abdul Malik, G. Wilkinson, *J. Am. Chem. Soc.*, **101**, 4128 (1979).
16. J. Plank, D. Riedel, W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, **19**, 937 (1980).
17. N. M. Boag, M. Green, F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1281 (1980).

1.10.6.2. of Metal Anions

1.10.6.2.1. Which are Mononuclear: Scope.

This widely used method is, just like the protonation of neutral complexes, a formal oxidative addition requiring a d-electron configuration between d^2 and d^{10} . In practice, most applications are to d-electron configurations between d^6 and d^{10} (see Table 1).

Most transition-metal anions give hydrides by protonation at the metal, but acyl anions generally give hydroxycarbene complexes instead of acyl hydrides¹⁸⁻²¹:



Because the charge on the acyl anion is localized at the acyl oxygen, protonation at that oxygen can occur with little electronic rearrangement, and O-protonation is favored kinetically. It is not clear whether hydroxycarbene complexes are more stable than acyl hydrides²².

Just as further protonation of a cationic hydride can lead to H_2 evolution and formation of a dication, further protonation of a neutral hydride can lead to H_2 loss and formation of a monocation. Although $\text{CF}_3\text{SO}_3\text{H}$ in THF gives²³ $\text{HMn}(\text{CO})_5$ from $[\text{Mn}(\text{CO})_5]^-$:

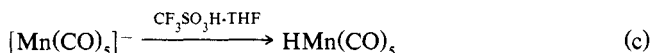
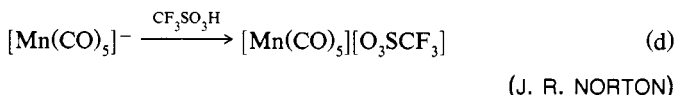


TABLE 1. FORMATION OF HYDRIDES BY PROTONATION OF ANIONIC TRANSITION-METAL COMPLEXES

Anion (d-electron configuration)	Acid	Hydride (d-electron configuration)	Refs.
$K_3[W(CN)_7]$ (d^4)	HOAc	$K_4[W(CN)_7H]$ (d^3)	1
$Na[h^5-C_5H_5Mo(CO)_3]$ (d^6)	HOAc	$h^5-C_5H_5Mo(CO)_3H$ (d^4)	2-5
$Na_2[h^5-C_5H_5Nb(CO)_3]$ (d^6)	CH_3CN	$Na[h^5-C_5H_5Nb(CO)_3H]$ (d^4)	6
$Na_3V(CO)_5$ (d^3)	$EtOH^a$	$Na_3[HV(CO)_5]$ (d^6)	7
$Na[Re(CO)_5]$ (d^8)	H_3PO_4	$HRe(CO)_5$ (d^6)	5, 8, 9
$Na[h^5-C_5H_5Fe(CO)_2]$ (d^8)	HOAc	$h^5-C_5H_5Fe(CO)_2H$ (d^6)	10
$K[h^5-C_5Me_5Ru(CO)_2]$ (d^8)	HOAc	$h^5-C_5Me_5Ru(CO)_2H$ (d^6)	11
$K[HFe(CO)_4]$ (d^8)	H_2SO_4	$H_2Fe(CO)_4$ (d^6)	12
$[Co(py)_6][Co(CO)_4]_2$ (d^{10})	H_2SO_4	$HCo(CO)_4$ (d^8)	13, 14
$K[Rh(PF_3)_4]$ (d^{10})	H_2SO_4 or H_3PO_4	$HRh(PF_3)_4$ (d^8)	15
$Na_2Os(CO)_4$ (d^{10})	H_3PO_4	$H_2Os(CO)_4$ (d^6)	16, 17

^a In liq NH_3 at $-50^\circ C$.

further reaction occurs²⁴ in neat CF_3SO_3H :



1. A. M. Soares, P. M. Kiernan, D. J. Cole-Hamilton, W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 84 (1981).
2. T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).
3. R. B. King, F. G. A. Stone, *Inorg. Synth.*, 7, 107 (1963).
4. E. O. Fischer, *Inorg. Synth.*, 7, 136 (1963).
5. R. B. King, *Organometallic Synthesis*, Vol. 1, Academic Press, New York, 1965.
6. F. Nümann, D. Rehder, V. Pank, *J. Organomet. Chem.*, 240, 363 (1982).
7. G. F. P. Warnock, S. B. Philson, J. E. Ellis, *J. Chem. Soc., Chem. Commun.*, 893 (1984).
8. W. Beck, W. Hieber, G. Braun, *Z. Anorg. Allg. Chem.*, 308, 23 (1961).
9. B. H. Byers, T. L. Brown, *J. Am. Chem. Soc.*, 98, 2527 (1977).
10. S. B. Ferguson, L. J. Sanderson, T. A. Shakelton, M. C. Baird, *Inorg. Chim. Acta*, 83, L45 (1984).
11. A. Stasunik, D. R. Wilson, W. Malisch, *J. Organomet. Chem.*, 270, C18 (1984).
12. L. Vancea, W. A. G. Graham, *J. Organomet. Chem.*, 134, 219 (1971).
13. H. W. Sternberg, I. Wender, M. Orchin, *Inorg. Synth.*, 5, 192 (1957).
14. R. J. Clark, S. E. Whiddon, R. E. Serfass, *J. Organomet. Chem.*, 11, 637 (1968).
15. T. Kruck, W. Lang, N. Derner, M. Stadler, *Chem. Ber.*, 101, 3816 (1968).
16. R. D. George, S. A. R. Knox, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 972 (1973).
17. J. Evans, J. R. Norton, *J. Am. Chem. Soc.*, 96, 7577 (1974).
18. E. O. Fischer, A. Riedel, *Chem. Ber.*, 101, 156 (1968).
19. E. O. Fischer, G. Kreiss, F. R. Kreissl, *J. Organomet. Chem.*, 56, C37 (1973).
20. J. R. Moss, M. Green, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 975 (1973).
21. K. P. Darst, C. M. Lukehart, *J. Organomet. Chem.*, 171, 65 (1979).
22. M. J. Breen, P. M. Schulman, G. L. Geoffroy, A. L. Rheingold, W. C. Fultz, *Organometallics*, 3, 782 (1984).
23. J. A. Gladysz, W. Tam, G. M. Williams, D. L. Johnson, D. W. Parker, *Inorg. Chem.*, 18, 1163 (1979).
24. W. C. Troglor, *J. Am. Chem. Soc.*, 101, 6459 (1979).

214 1.10. Formation of Bonds between Hydrogen and Transition Metals
 1.10.6. by Protonation
 1.10.6.2. of Metal Anions

1.10.6.2.2. Which Are Mononuclear: Position of the Protonation Equilibria.

The available pK_a data derive from a variety of solvents. Values for representative hydride complexes are given in Table 1.

As can be seen by comparing $HCo(CO)_4$ with $HCo(CO)_3L$ and $HV(CO)_6$ with $HV(CO)_5L$, σ -donor ligands decrease the acidity of hydrides; the data¹⁸ on $HCo(CO)_3L$ and $HCoL_4$ show that phosphines decrease the acidity more than do phosphites. Comparison of $H_2Os(CO)_4$ and $H(CH_3)Os(CO)_4$ suggests that replacement of a hydride by an alkyl also decreases acidity.

Acidity usually decreases down a periodic column, e.g., the acidity of $h^5C_5H_5-M(CO)_3H$ decreases $Cr > Mo > W$; $H_2Os(CO)_4$ is a weaker acid than $H_2Fe(CO)_4$ and $HRe(CO)_5$ cannot be deprotonated¹⁹ under the conditions employed for the titration and pK_a determination of $HMn(CO)_5$. However, there is little difference in pK_a between the Co and Rh dimethylglyoxime complexes (see Table 1), and IR observations

TABLE 1. ACIDITY OF NEUTRAL AND ANIONIC TRANSITION-METAL HYDRIDES

Hydride	pK_a	Solvent ^a	Refs.
$HMn(CO)_5$	7.1	H_2O (20°C)	1
$HMn(CO)_5$	15.1	CH_3CN	2
$HRe(CO)_5$	ca. 22	CH_3CN	2
$H_2Fe(CO)_4$	4.00 (pK_1) 12.68 (pK_2)	H_2O (20°C)	7
$H_2Fe(CO)_4$	5.88 (pK_1)	70% aq MeOH	4
$H_2Fe(CO)_4$	11.4 (pK_1)	CH_3CN	2
$H_2Os(CO)_4$	15.2	MeOH	5
$H_2Os(CO)_4$	20.8	CH_3CN	6
$H(CH_3)Os(CO)_4$	23.0	CH_3CN (0°C)	6
$HCo(CO)_4$	Strong acid	H_2O	7
$HCo(CO)_4$	Strong acid	MeOH (0°C)	7
$HCo(CO)_4$	8.4	CH_3CN	8
$HCo(CO)_3P(OPh)_3$	4.95	H_2O	9
$HCo(CO)_3P(OPh)_3$	11.4	CH_3CN	8
$HCo(CO)_3PPh_3$	6.96	H_2O	9
$HCo(CO)_3PPh_3$	15.4	CH_3CN	8
$HV(CO)_6$	Strong acid	H_2O	10, 11
$HV(CO)_5PPh_3$	6.8	H_2O	10
$h^5-C_5H_5Cr(CO)_3H$	13.3	CH_3CN	6
$h^5-C_5H_5Mo(CO)_3H$	13.9	CH_3CN (0°C)	6
$h^5-C_5H_5W(CO)_3H$	16.1	CH_3CN	6
$h^5-C_5H_5W(CO)_3H$	9.0	MeOH	12
$h^5-C_5H_5W(CO)_2(PMe_3)H^b$	26.6	CH_3CN	2
$h^5-C_5H_5Fe(CO)_2H$	19.4	CH_3CN	2
$h^5-C_5Me_5Fe(CO)_2H$	26.3	CH_3CN	2
$h^5-C_5H_5Ru(CO)_2H$	20.2	CH_3CN	2
$HCo(DMGH)_2PBu_3^c$	10.5	H_2O -MeOH	13
$HRh(DMGH)_2PPh_3^c$	9.5	H_2O -MeOH	14, 15
$[HCo(CN)_5]^{1-}$	20	H_2O	16, 17

^a Temperature 25°C unless otherwise stated.

^b Rapidly equilibrating mixture of cis- and trans-isomers.

^c DMGH = dimethylglyoximate monoanion.

under high CO pressure in solution²⁰ suggest the order of basicities $[\text{Rh}(\text{CO})_4]^- < [\text{Co}(\text{CO})_4]^- < [\text{Ir}(\text{Co})_4]^-$. Conductivity-based estimates²¹ of the basicity of the PF_3 analogues in acetone give the order $[\text{Co}(\text{PF}_3)_4]^- \approx [\text{Rh}(\text{PF}_3)_4]^- < [\text{Ir}(\text{PF}_3)_4]^-$. The more acidic behavior in H_2O of $[\text{Rh}(\text{CN})_5\text{H}]^{3-}$ in comparison with $[\text{Co}(\text{CN})_5\text{H}]^{3-}$ is not a true pK_a difference but a reflection of the greater tendency of $[\text{Rh}(\text{CN})_5]^{4-}$ to dissociate²² to the four-coordinated complex, $[\text{Rh}(\text{CN})_4]^{3-}$.

Some hydrides are strong acids, and the protonation of their anions is correspondingly difficult. The equilibria in Table 1 indicate that acetic acid is not strong enough to protonate some anions (the pK_a of acetic acid²³ in acetonitrile is 22.3), and it should be avoided except where experience shows that it is satisfactory. The hydrides $\text{HM}(\text{PF}_3)_4$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) are all strong acids in H_2O -acetone, and their preparation from the corresponding anions requires 50% sulfuric or phosphoric acid.²¹

Some group IVB ligands cause hydrides to become acidic; e.g., $\text{h}^5\text{-C}_5\text{H}_5\text{-Fe}(\text{CO})(\text{SiCl}_3)_2\text{H}$ has²⁴ a pK_a of 2.6 in CH_3CN . Less strong but still deprotonated by Et_3N in CH_2Cl_2 are $\text{H}(\text{Cl}_3\text{Si})\text{Fe}(\text{CO})_4$, $\text{H}(\text{Ph}_3\text{Si})\text{Fe}(\text{CO})_4$ and $\text{H}(\text{Cl}_3\text{Si})\text{Mn}(\text{CO})_2\text{C}_5\text{H}_5\text{-h}^5$; their acidity decreases in the order given,²⁴ and $\text{H}(\text{Ph}_3\text{Ge})\text{Fe}(\text{CO})_4$ is sufficiently acidic to be deprotonated by Cl^- in CH_2Cl_2 . Protonation of $[\text{Et}_4\text{N}][\text{Ph}_3\text{GeFe}(\text{CO})_4]$ nevertheless can be accomplished²⁵ by HCl in Et_2O -THF because of the low solubility of the resulting Et_4NCl .

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3. F. Galembeck, P. Krumholz, *J. Am. Chem. Soc.*, **43**, 1939 (1971).
4. R. G. Pearson, H. Mauermann, *J. Am. Chem. Soc.*, **104**, 500 (1983).
5. H. W. Walker, R. G. Pearson, P. C. Ford, *J. Am. Chem. Soc.*, **105**, 1179 (1983).
6. R. F. Jordan, J. R. Norton, *J. Am. Chem. Soc.*, **104**, 1255 (1982).
7. W. Hieber, W. Hubel, *Z. Elektrochem.*, **57**, 235 (1953).
8. E. J. Moore, J. R. Norton, unpublished work, 1985.
9. W. Hieber, E. Lindner, *Chem. Ber.*, **94**, 1417 (1961).
10. W. Hieber, E. Winter, and E. Schubert, *Chem. Ber.*, **95**, 3070 (1962).
11. F. Calderazzo, G. Pompaloni, D. Vitali, *Gazz. Chem. Ital.*, **111**, 455 (1981).
12. C. Amman, R. G. Pearson, unpublished work, quoted in R. G. Pearson, *Chem. Rev.*, **85**, 41 (1985).
13. G. N. Schrauzer, R. J. Holland, *J. Am. Chem. Soc.*, **93**, 1505 (1971).
14. J. H. Weber, G. N. Schrauzer, *J. Am. Chem. Soc.*, **92**, 726 (1970).
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18. H.-F. Klein, *Angew. Chem., Int. Ed. Engl.*, **19**, 362 (1980).
19. W. Beck, W. Hieber, G. Braun, *Z. Anorg. Allg. Chem.*, **308**, 23 (1961).
20. J. L. Vidal, W. E. Walker, *Inorg. Chem.*, **20**, 249 (1981).
21. T. Kruck, W. Lang, N. Derner, M. Stadler, *Chem. Ber.*, **101**, 3816 (1968).
22. J. Halpern, R. Cozens, L.-Y. Goh, *Inorg. Chim. Acta*, **12**, L35 (1975).
23. I. M. Kolthoff, M. K. Chantooni, S. Bhowmik, *J. Am. Chem. Soc.*, **90**, 23 (1968).
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1.10.6.2.3. Which Are Mononuclear: Rates.

Proton transfers to metal anions are much slower (see Table 1) than proton transfers to other bases of comparable thermodynamic strength, reflecting the extent of the electronic rearrangement that must occur on protonation of a metal anion^{3,4}. A kinetic-

1.10. Formation of Bonds between Hydrogen and Transition Metals 215

1.10.6. by Protonation

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6. R. F. Jordan, J. R. Norton, *J. Am. Chem. Soc.*, **104**, 1255 (1982).
7. W. Hieber, W. Hubel, *Z. Elektrochem.*, **57**, 235 (1953).
8. E. J. Moore, J. R. Norton, unpublished work, 1985.
9. W. Hieber, E. Lindner, *Chem. Ber.*, **94**, 1417 (1961).
10. W. Hieber, E. Winter, and E. Schubert, *Chem. Ber.*, **95**, 3070 (1962).
11. F. Calderazzo, G. Pompaloni, D. Vitali, *Gazz. Chem. Ital.*, **111**, 455 (1981).
12. C. Amman, R. G. Pearson, unpublished work, quoted in R. G. Pearson, *Chem. Rev.*, **85**, 41 (1985).
13. G. N. Schrauzer, R. J. Holland, *J. Am. Chem. Soc.*, **93**, 1505 (1971).
14. J. H. Weber, G. N. Schrauzer, *J. Am. Chem. Soc.*, **92**, 726 (1970).
15. T. Ramasami, J. H. Espenson, *Inorg. Chem.*, **19**, 1846 (1980).
16. H. S. Lim, F. C. Anson, *Inorg. Chem.*, **10**, 103 (1971).
17. G. D. Venerable II, J. Halpern, *J. Am. Chem. Soc.*, **93**, 2176 (1971).
18. H.-F. Klein, *Angew. Chem., Int. Ed. Engl.*, **19**, 362 (1980).
19. W. Beck, W. Hieber, G. Braun, *Z. Anorg. Allg. Chem.*, **308**, 23 (1961).
20. J. L. Vidal, W. E. Walker, *Inorg. Chem.*, **20**, 249 (1981).
21. T. Kruck, W. Lang, N. Derner, M. Stadler, *Chem. Ber.*, **101**, 3816 (1968).
22. J. Halpern, R. Cozens, L.-Y. Goh, *Inorg. Chim. Acta*, **12**, L35 (1975).
23. I. M. Kolthoff, M. K. Chantooni, S. Bhowmik, *J. Am. Chem. Soc.*, **90**, 23 (1968).
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1.10.6.2.3. Which Are Mononuclear: Rates.

Proton transfers to metal anions are much slower (see Table 1) than proton transfers to other bases of comparable thermodynamic strength, reflecting the extent of the electronic rearrangement that must occur on protonation of a metal anion^{3,4}. A kinetic-

TABLE 1. RATES OF PROTONATION OF MONONUCLEAR ANIONS AT 25°C

Anion	Acid	Solvent	k	Refs.
$[\text{Co}(\text{CN})_5]^{4-}$	H_2O	H_2O	$1.1 \times 10^5 \text{ s}^{-1} (20^\circ\text{C})$	1
$[\text{Rh}(\text{DMGH})_2\text{PPh}_3]^{-a}$	$[\text{H}_3\text{O}]^+$	$\text{H}_2\text{O}-\text{MeOH}$	$36 \text{ M}^{-1} \text{ s}^{-1}$	2
$[\text{HOs}(\text{CO})_4]^-$	CH_3OH	CH_3OH	0.8 s^{-1}	3
$[\text{HOs}(\text{CO})_4]^-$	$[\text{Et}_3\text{NH}]^+$	CH_3CN	$1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	4
$[\text{HOs}(\text{CO})_4]^-$	$\text{H}_2\text{Os}(\text{CO})_4$	CH_3CN	$0.075 \text{ M}^{-1} \text{ s}^{-1} (30^\circ\text{C})$	4
$[\text{CH}_3\text{Os}(\text{CO})_4]^-$	$[\text{Et}_3\text{NH}]^+$	CH_3CN	$1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	4
$[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]^-$	$[\text{morH}]^+b$	CH_3CN	$5.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	4
$[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]^-$	$\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$	CH_3CN	$650 \text{ M}^{-1} \text{ s}^{-1}$	4, 5
$[\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]^-$	$\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$	CH_3CN	$2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	4, 5
$[\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$	$\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{H}$	CH_3CN	$1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	4, 5

^a DMGH = dimethylglyoximate monoanion.

^b mor = morpholine.

isotope effect of 5.8 is observed¹ on replacing H_2O by D_2O in the protonation of $[\text{Co}(\text{CN})_5]^{4-}$.

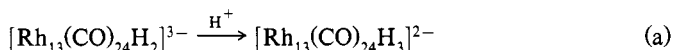
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3. H. W. Walker, R. G. Pearson, P. C. Ford, *J. Am. Chem. Soc.*, **105**, 1179 (1983).
4. R. F. Jordan, J. R. Norton, *J. Am. Chem. Soc.*, **104**, 1255 (1982).
5. J. M. Sullivan, J. R. Norton, unpublished work, 1985.

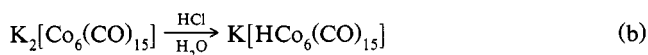
1.10.6.2.4. Which Are Polynuclear.

Polynuclear anions are generated readily, and some polynuclear hydrides that can be made by this method¹⁻³ are listed⁴⁻¹² in Table 1. Although these anions are isolated and characterized, polynuclear hydrides frequently are made from anions prepared in situ. As with the cationic polynuclear hydrides discussed previously, the location of the H atom may be unknown, even though the ^1H NMR specifies that it is attached to the metal core.

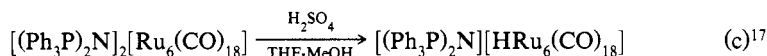
In the hexagonally close-packed Rh anions¹³⁻¹⁵, $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{5-n}]^{n-}$, where $n = 2-4$, protonation, instead of occurring at any specific Rh atoms or Rh—Rh bond, inserts an additional interstitial hydrogen atom:



Similar interstitial hydrogens are obtained on protonation¹⁶ of $[\text{Co}_6(\text{CO})_{15}]^{2-}$:



and $[\text{Ru}_6(\text{CO})_{18}]^{2-}$:



A large kinetic-isotope effect on protonation rates of polynuclear anions indicate

216 1.10. Formation of Bonds between Hydrogen and Transition Metals
 1.10.6. by Protonation
 1.10.6.2. of Metal Anions

TABLE 1. RATES OF PROTONATION OF MONONUCLEAR ANIONS AT 25°C

Anion	Acid	Solvent	k	Refs.
$[\text{Co}(\text{CN})_5]^{4-}$	H_2O	H_2O	$1.1 \times 10^5 \text{ s}^{-1}$ (20°C)	1
$[\text{Rh}(\text{DMGH})_2\text{PPh}_3]^{-a}$	$[\text{H}_3\text{O}]^+$	$\text{H}_2\text{O}-\text{MeOH}$	$36 \text{ M}^{-1} \text{ s}^{-1}$	2
$[\text{HOs}(\text{CO})_4]^-$	CH_3OH	CH_3OH	0.8 s^{-1}	3
$[\text{HOs}(\text{CO})_4]^-$	$[\text{Et}_3\text{NH}]^+$	CH_3CN	$1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	4
$[\text{HOs}(\text{CO})_4]^-$	$\text{H}_2\text{Os}(\text{CO})_4$	CH_3CN	$0.075 \text{ M}^{-1} \text{ s}^{-1}$ (30°C)	4
$[\text{CH}_3\text{Os}(\text{CO})_4]^-$	$[\text{Et}_3\text{NH}]^+$	CH_3CN	$1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	4
$[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]^-$	$[\text{morH}]^+b$	CH_3CN	$5.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	4
$[\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3]^-$	$\text{h}^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$	CH_3CN	$650 \text{ M}^{-1} \text{ s}^{-1}$	4, 5
$[\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]^-$	$\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$	CH_3CN	$2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	4, 5
$[\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$	$\text{h}^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{H}$	CH_3CN	$1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	4, 5

^a DMGH = dimethylglyoximate monoanion.

^b mor = morpholine.

isotope effect of 5.8 is observed¹ on replacing H_2O by D_2O in the protonation of $[\text{Co}(\text{CN})_5]^{4-}$.

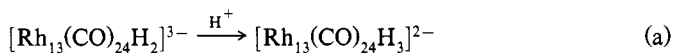
(J. R. NORTON)

1. G. D. Venerable II, J. Halpern, *J. Am. Chem. Soc.*, **93**, 2176 (1971).
2. T. Ramasami, J. H. Espenson, *Inorg. Chem.*, **19**, 1846 (1980).
3. H. W. Walker, R. G. Pearson, P. C. Ford, *J. Am. Chem. Soc.*, **105**, 1179 (1983).
4. R. F. Jordan, J. R. Norton, *J. Am. Chem. Soc.*, **104**, 1255 (1982).
5. J. M. Sullivan, J. R. Norton, unpublished work, 1985.

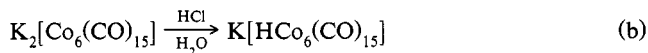
1.10.6.2.4. Which Are Polynuclear.

Polynuclear anions are generated readily, and some polynuclear hydrides that can be made by this method¹⁻³ are listed⁴⁻¹² in Table 1. Although these anions are isolated and characterized, polynuclear hydrides frequently are made from anions prepared in situ. As with the cationic polynuclear hydrides discussed previously, the location of the H atom may be unknown, even though the ¹H NMR specifies that it is attached to the metal core.

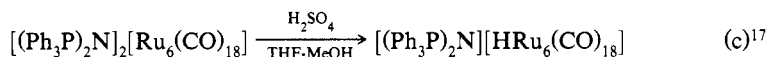
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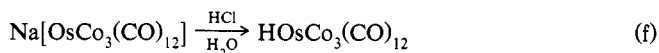
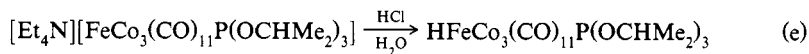
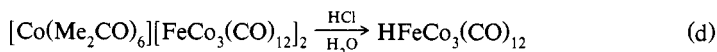


A large kinetic-isotope effect on protonation rates of polynuclear anions indicate

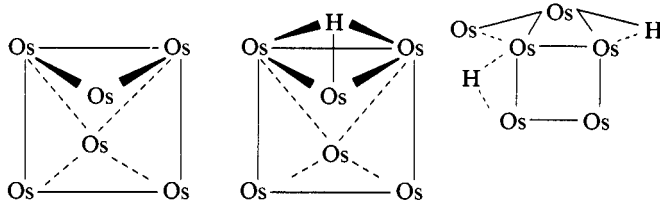
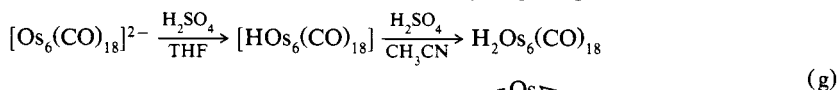
TABLE 1. FORMATION OF POLYNUCLEAR HYDRIDES BY PROTONATION OF POLYNUCLEAR ANIONS

Anion	Acid	Hydride	Refs.
$\text{Na}_2[\text{Fe}_2(\text{CO})_8]$	$\text{HOAc-EtOH}-(\text{Ph}_3\text{P})_2\text{N}$	$(\text{Ph}_3\text{P})_2\text{N}[\text{HFe}_2(\text{CO})_8]$	4, 5
$[\text{Et}_4\text{N}][\text{Cr}_2(\text{CO})_{10}]$	$\text{HCl-THF-Et}_2\text{O}$	$[\text{Et}_4\text{N}][\text{HCr}_2(\text{CO})_{10}]$	6
$\text{K}_2[\text{Ru}_4(\text{CO})_{13}]$	HCl (1 equiv)-THF	$\text{K}[\text{HRu}_4(\text{CO})_{13}]$	7
$\text{K}_2[\text{Ru}_4(\text{CO})_{13}]$	$\text{H}_2\text{SO}_4\text{-THF}$	$\text{H}_2\text{Ru}_4(\text{CO})_{13}$	7
$\text{K}_4[\text{Ru}_4(\text{CO})_{12}]$	H_2SO_4	$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	7
$\text{K}[\text{CoRu}_3(\text{CO})_{13}]$	$\text{H}_2\text{SO}_4\text{-hexane}$	$\text{HCoRu}_3(\text{CO})_{13}$	8
$[\text{Me}_4\text{N}][\text{MnOs}_2(\text{CO})_{12}]$	$\text{H}_3\text{PO}_4\text{-acetone}$	$\text{HMnOs}_2(\text{CO})_{12}$	9
$[\text{Et}_4\text{N}][\text{Fe}_4\text{N}(\text{CO})_{12}]$	$\text{H}_2\text{SO}_4\text{-toluene}$	$\text{HFe}_4\text{N}(\text{CO})_{12}$	10
$[\text{Et}_4\text{N}][\text{Fe}_5\text{N}(\text{CO})_{14}]$	$\text{H}_2\text{SO}_4\text{-toluene}$	$\text{HFe}_5\text{N}(\text{CO})_{14}$	10
$[\text{Mo}_2\text{Cl}_8]^{4-}$	$\text{HCl-H}_2\text{O}$	$[\text{HMo}_2\text{Cl}_8]^{3-}$	11, 12

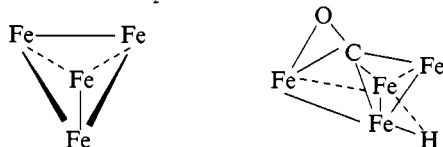
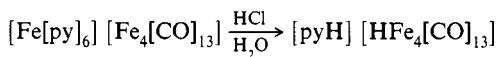
that the proton is becoming an interstitial hydrogen¹⁸, but such kinetic-isotope effects occur generally in the protonation of polynuclear complexes. Reactions (d), (e) and (f) show $k_{\text{H}}/k_{\text{D}}$ values of 16.8, 8.3 and 16.2, respectively¹⁸⁻²⁰:



Some polynuclear anions change the structure of their metal cores on protonation. For example, the dianion $[\text{Os}_6(\text{CO})_{18}]^{2-}$ has O_h symmetry; the first proton bridges an O_h face, and the second causes the metal framework to rearrange to a monocapped square pyramid in which the exact location of the hydrogen ligands is not clear^{21,22}:



Protonation of $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ changes the core geometry from T_d to a butterfly arrangement in which a carbonyl group behaves as a four-electron donor^{23,24}:



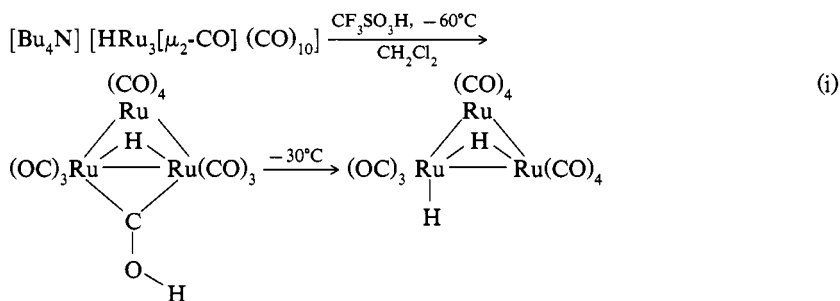
(h)

A similar rearrangement occurs when $[(\text{Ph}_3\text{P})_2\text{N}][\text{Fe}_4(\text{CO})_{12}\text{COMe}]$ is protonated, giving^{25,26} $\text{HFe}_4(\text{CO})_{12}\text{COMe}$.

Such structural differences between anion and hydride may be a factor in the high acidity of some polynuclear hydrides and the consequent difficulty of forming them by protonation of their anions. However, a more general cause is probably the delocalization of charge over several metal centers and π -acceptor ligands; e.g., $[\text{HCo}_6(\text{CO})_{15}]^-$ is deprotonated by THF, H_2O , acetone and alcohols (although equilibration in alcohols requires¹⁶ about an hour). Its formation in reaction (b), therefore, requires strong acid; there is no evidence for diprotonation. Similarly, the second protonation in reaction (g) succeeds only when a solvent (CH_3CN) is used in which the neutral dihydride is insoluble²¹. Other examples of anions for which attempts at isolating a protonated derivative have failed are: $[\text{Cr}_2(\text{CO})_{10}]^{2-}$,⁶ $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ ² and $[\text{Re}_4(\text{CO})_{16}]^{2-}$.²⁷ The proton basicity of anions increases markedly with increasing charge per metal: the pK_a of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ in H_2O is 3, that of $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$ is 10, and that of $[\text{HRe}_3(\text{CO})_{12}]^{2-}$ is^{28,25} 25.

The same factors (structural rearrangement on protonation and delocalization of negative charge) that produce the low proton basicity of polynuclear anions are probably also responsible for the slow rate at which protonation equilibria are established with polynuclear systems²⁸⁻³⁰ (see Table 2). If $[\text{HOs}(\text{CO})_4\text{Os}(\text{CO})_4]^-$ is compared with the mononuclear Os anions in the previous two subsections, it is clear that the second $\text{Os}(\text{CO})_4$ unit has decreased the rate of protonation as well as the proton basicity.

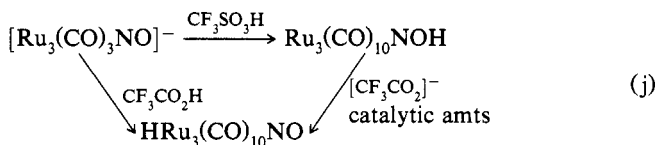
The interplay of these kinetic and thermodynamic factors determines the site of protonation (i.e., metal core or ligand) of polynuclear anions. The Fe_2H hydrogen in $\text{HFe}_4(\text{CH-h}^2)(\text{CO})_{12}$ is both kinetically and thermodynamically less acidic than the $\text{h}^2\text{-CH}$ one³¹. The reaction of CH_3CN with Fe-carbonyl anion systems under protic conditions occurs by initial kinetically controlled protonation at nitrogen, forming $[\text{Fe}_3(\text{CO})_9\text{CH}_3\text{C}=\text{NH}]^-$; this is followed by protonation of the weakly basic Fe core and movement of the ligand proton from nitrogen to the thermodynamically more basic carbon to form³² $\text{HFe}_3(\text{N}=\text{CHCH}_3)(\text{CO})_9$. Kinetic vs. thermodynamic control of the site of protonation is illustrated by³³:



The oxygen of the $\mu_2\text{-CO}$ is the kinetically preferred site of protonation (the analogous Fe_3 compound can be isolated³⁴), but protonation of the Ru_3 core is favored thermodynamically [the analogous Os_3 compound is obtained³⁵ on protonation of $[\text{HOs}_3(\mu_2\text{-CO})(\text{CO})_{10}]^-$ at RT]. Similarly, $[\text{Ru}_3(\text{CO})_{10}\text{NO}]^-$ undergoes kinetic protonation (e.g., by the strong acid $\text{CF}_3\text{SO}_3\text{H}$) on the nitrosyl oxygen, but thermodynamic protonation (e.g., by the weaker acid, $\text{CF}_3\text{CO}_2\text{H}$) in the presence of an anion that catalyzes the attainment of equilibrium on the Ru_3 core³⁶:

TABLE 2. RATE AND EQUILIBRIUM DATA FOR PROTONATION OF POLYNUCLEAR ANIONS

Anion	pK _a (solvent), 25°C	Acid	Protonation rate, 25°C	Refs.
[H ₃ Ru ₄ (CO) ₁₂] ⁻	11.7 (MeOH)	MeOH	0.08 s ⁻¹	29
[H ₃ FeRu ₃ (CO) ₁₂] ⁻	11.8 (MeOH)	MeOH	0.1 s ⁻¹	29
[HRu ₄ (CO) ₁₃] ⁻	11.1 (MeOH)	MeOH	0.02 s ⁻¹	29
[HFeRu ₃ (CO) ₁₃] ⁻	11.2 (MeOH)	MeOH	0.05 s ⁻¹	29
[H ₃ Os ₄ (CO) ₁₂] ⁻	12.3 (MeOH)	MeOH	0.1 s ⁻¹	29
[HOS ₂ (CO) ₈] ⁻	20.4 (CH ₃ CN)	[Et ₃ NH] ⁺	8 × 10 ² M ⁻¹ s ⁻¹	30



(J. R. NORTON)

1. A. P. Humphries, H. D. Kaesz, *Prog. Inorg. Chem.*, **25**, 145 (1979); a comprehensive review of polynuclear hydrides, including a section on their formation by protonation of polynuclear anions.
2. P. Chini, G. Longoni, V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976); although confined to clusters containing five or more metal atoms, a good general discussion of synthetic methods for polynuclear carbonyl anions.
3. D. A. Roberts, G. L. Geoffroy, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, 1982, Ch. 40; although confined to heterometallic systems, a good general discussion of synthetic methods for polynuclear carbonyl anions.
4. J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 1119 (1978).
5. H. B. Chin, R. Bau, *Inorg. Chem.*, **17**, 2314 (1978).
6. R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).
7. C. C. Nagel, S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 530 (1980).
8. P. C. Steinhardt, W. L. Gladfelter, A. D. Harley, J. R. Fox, G. L. Geoffrey, *Inorg. Chem.*, **19**, 332 (1980).
9. J. Knight, M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1022 (1972).
10. M. Tachikawa, J. Stein, E. L. Muetterties, R. G. Teller, M. A. Beno, E. Gebert, J. M. Williams, *J. Am. Chem. Soc.*, **102**, 6649 (1980).
11. F. A. Cotton, P. C. W. Leung, W. J. Roth, A. J. Schultz, J. M. Williams, *J. Am. Chem. Soc.*, **106**, 117 (1984).
12. S. S. Miller, A. Haim, *J. Am. Chem. Soc.*, **105**, 5624 (1983).
13. V. G. Albano, A. Ceriotti, P. Chini, G. Chiani, S. Martinengo, W. M. Anker, *J. Chem. Soc., Chem. Commun.*, 859 (1975).
14. V. G. Albano, G. Ciani, S. Martinengo, A. Sironi, *J. Chem. Soc., Dalton Trans.*, 978 (1979).
15. G. Ciani, A. Sironi, S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 519 (1981).
16. D. W. Hart, R. G. Teller, C.-Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, T. F. Koetzle, *J. Am. Chem. Soc.*, **103**, 1458 (1981).
17. C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 383 (1980).
18. M. J. Mays, R. N. F. Simpson, *J. Chem. Soc., A*, 1444 (1968).
19. J. Knight, M. J. Mays, *J. Chem. Soc., A*, 711 (1970).
20. C. G. Cooke, M. J. Mays, *J. Organomet. Chem.*, **74**, 449 (1974).
21. C. R. Eady, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Chem. Commun.*, 302 (1976).
22. M. McPartlin, C. R. Eady, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Chem. Commun.*, 883 (1976).

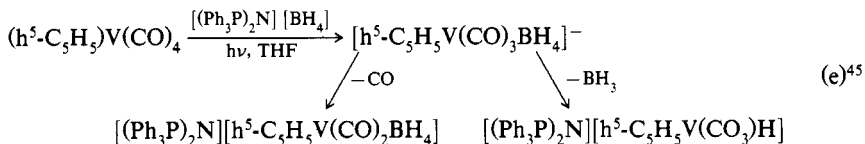
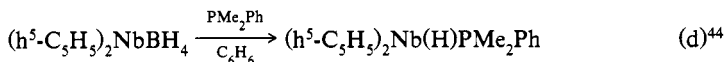
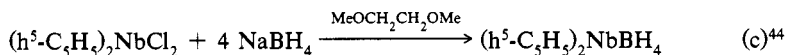
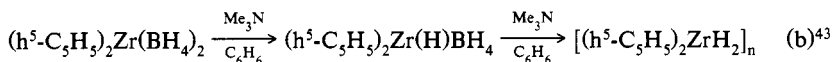
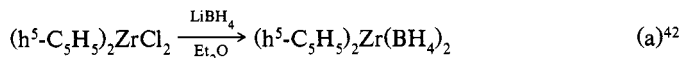
23. W. Hieber, R. Werner, *Chem. Ber.*, **90**, 286 (1957).
24. M. Manassero, M. Sansoni, G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).
25. E. M. Holt, K. H. Whitmire, D. F. Shriver, *J. Organomet. Chem.*, **213**, 125 (1981).
26. E. M. Holt, K. H. Whitmire, D. F. Shriver, *J. Am. Chem. Soc.*, **104**, 5621 (1982).
27. R. Bau, B. Fontal, H. D. Kaesz, M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 6374 (1967).
28. H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).
29. H. W. Walker, R. G. Pearson, P. C. Ford, *J. Am. Chem. Soc.*, **105**, 1179 (1983).
30. R. F. Jordan, J. R. Norton, *J. Am. Chem. Soc.*, **104**, 1255 (1982).
31. M. Tachikawa, E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980).
32. M. A. Andrews, H. D. Kaesz, *J. Am. Chem. Soc.*, **101**, 7238 (1979).
33. J. B. Keister, *J. Organomet. Chem.*, **190**, C36 (1980).
34. H. A. Hodali, D. F. Shriver, *Inorg. Chem.*, **18**, 1236 (1979).
35. C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, *J. Chem. Soc., Dalton Trans.*, 1358 (1978).
36. R. E. Stevens, W. L. Gladfelter, *J. Am. Chem. Soc.*, **104**, 6454 (1982).

1.10.7. by Reduction of Metal Complexes

1.10.7.1. with Borohydride.

This is a common method for preparing transition-metal hydrides (see Table 1)¹⁻⁷.

Borohydride reduction is complex, e.g., $\text{Ru}_3(\text{CO})_{12}$ with NaBH_4 in THF gives over a dozen products⁴¹, but a few useful mechanistic generalizations can be offered. Syntheses of metal hydrides proceed through intermediate borohydride complexes. Electron-pair bases (an ethereal solvent may be sufficient) are then necessary to complex and remove BH_3 . In a few examples the borohydride complexes are observable:



In Eq. (e), an intermediate, coordinatively saturated monodentate borohydride complex, $[\text{h}^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{BH}_4]^-$, is formed, which can either lose CO to give a bidentate borohydride complex or lose BH_3 to give an anionic hydride⁴⁵. Similarly, the borohydride reduction of $\text{Mo}(\text{CO})_6$ in THF proceeds through an $[\text{Mo}(\text{CO})_5(\text{BH}_4)]^-$ intermediate that can either lose CO to form $[\text{Mo}(\text{CO})_4(\text{BH}_4)]^-$ or lose BH_3 to form $[\text{HMo}_2(\text{CO})_{10}]^-$. Diethyl ether (a weaker electron-pair donor) instead of THF favors

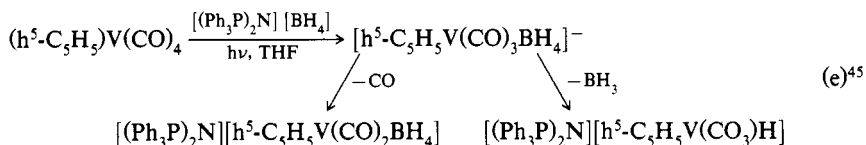
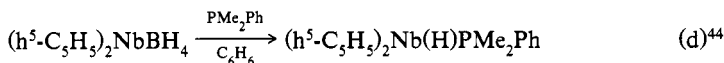
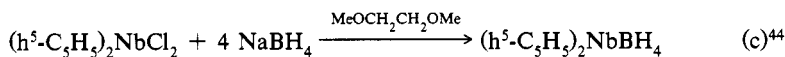
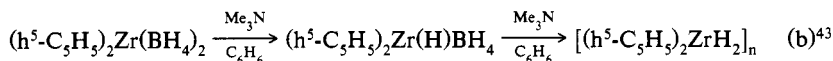
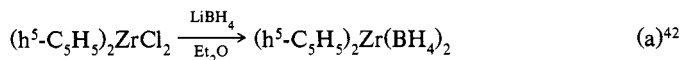
220 1.10. Formation of Bonds between Hydrogen and Transition Metals

23. W. Hieber, R. Werner, *Chem. Ber.*, **90**, 286 (1957).
24. M. Manassero, M. Sansoni, G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).
25. E. M. Holt, K. H. Whitmire, D. F. Shriver, *J. Organomet. Chem.*, **213**, 125 (1981).
26. E. M. Holt, K. H. Whitmire, D. F. Shriver, *J. Am. Chem. Soc.*, **104**, 5621 (1982).
27. R. Bau, B. Fontal, H. D. Kaesz, M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 6374 (1967).
28. H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973).
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30. R. F. Jordan, J. R. Norton, *J. Am. Chem. Soc.*, **104**, 1255 (1982).
31. M. Tachikawa, E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980).
32. M. A. Andrews, H. D. Kaesz, *J. Am. Chem. Soc.*, **101**, 7238 (1979).
33. J. B. Keister, *J. Organomet. Chem.*, **190**, C36 (1980).
34. H. A. Hodali, D. F. Shriver, *Inorg. Chem.*, **18**, 1236 (1979).
35. C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, *J. Chem. Soc., Dalton Trans.*, 1358 (1978).
36. R. E. Stevens, W. L. Gladfelter, *J. Am. Chem. Soc.*, **104**, 6454 (1982).

1.10.7. by Reduction of Metal Complexes**1.10.7.1. with Borohydride.**

This is a common method for preparing transition-metal hydrides (see Table 1)¹⁻⁷.

Borohydride reduction is complex, e.g., $\text{Ru}_3(\text{CO})_{12}$ with NaBH_4 in THF gives over a dozen products⁴¹, but a few useful mechanistic generalizations can be offered. Syntheses of metal hydrides proceed through intermediate borohydride complexes. Electron-pair bases (an ethereal solvent may be sufficient) are then necessary to complex and remove BH_3 . In a few examples the borohydride complexes are observable:



In Eq. (e), an intermediate, coordinatively saturated monodentate borohydride complex, $[\text{h}^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{BH}_4]^-$, is formed, which can either lose CO to give a bidentate borohydride complex or lose BH_3 to give an anionic hydride⁴⁵. Similarly, the borohydride reduction of $\text{Mo}(\text{CO})_6$ in THF proceeds through an $[\text{Mo}(\text{CO})_5(\text{BH}_4)]^-$ intermediate that can either lose CO to form $[\text{Mo}(\text{CO})_4(\text{BH}_4)]^-$ or lose BH_3 to form $[\text{HMo}_2(\text{CO})_{10}]^-$. Diethyl ether (a weaker electron-pair donor) instead of THF favors

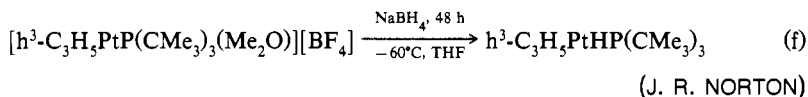
TABLE 1. PREPARATIONS OF TRANSITION-METAL HYDRIDES BY BOROHYDRIDE REDUCTION

Initial metal complex	Reagents and conditions	Product hydride	Refs.
WCl_6 or MoCl_5	$\text{NaC}_2\text{H}_5\text{-THF-NaBH}_4$ (initial mixing below -100°C followed by warming and brief reflux)	$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{MH}_2$ ($\text{M} = \text{W}$ or Mo)	8-10
TaCl_5	$\text{NaC}_2\text{H}_5\text{-THF-NaBH}_4$ (initial mixing at 0°C followed by warming and reflux)	$\text{h}^5\text{-C}_5\text{H}_5\text{-TaH}_3$	8
ReCl_5 W(CO)_6 W(CO)_6	$\text{NaC}_2\text{H}_5\text{-THF (}0^\circ\text{C), NaBH}_4$ (50°C) $\text{NaBH}_4\text{-THF}$ $[\text{Et}_4\text{N}][\text{BH}_4]\text{-THF}$ (reflux for several days)	$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{ReH}$ $[\text{HW}_2(\text{CO})_{10}]^-$ $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$	9, 11 12, 13 14
$\text{Re}_2(\text{CO})_{10}$ $\text{Re}_2(\text{CO})_{10}$	$\text{NaBH}_4\text{-THF-H}_3\text{PO}_4$ $\text{NaBH}_4\text{-THF}$ (reflux overnight followed by several days at RT)	$\text{H}_2\text{Re}_3(\text{CO})_{12}$ $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$	15, 16 17
$\text{Os}_8(\text{CO})_{18}$ $\text{WCl}_4(\text{PMc}_2\text{Ph})_2$ $\text{MoCl}_4(\text{PMcPh})_2$ $\text{MoCl}(\text{h}^5\text{-C}_5\text{H}_5)_2\text{PPh}_3\text{h}^6\text{-C}_6\text{H}_6$ $\text{ReCl}_3(\text{PMc}_2\text{Ph})_3$ $\text{Na}_2[\text{OsCl}_6] \cdot 6\text{H}_2\text{O}$ $\text{RuCl}_2[\text{P}(\text{OEt})_3]_4$ FeCl_2 $\text{h}^5\text{-C}_5\text{H}_5\text{Ru(PPh)}_3\text{Cl}$ $\text{Co}[\text{NO}]_2 \cdot 6\text{H}_2\text{O}$ CoCl_2 $\text{Na}_2[\text{IrCl}_6]$ $\text{trans-Ir(PPh)}_2(\text{CO})\text{Cl}$ $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ $\text{NiCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ $[\text{Pt}_2\text{Me}_2(\mu\text{-Cl})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2][\text{PF}_6]$ $\text{ClCo(DMGH)}_2\text{PPh}_3^a$ $\text{ClRh(DMGH)}_2\text{PPh}_3^a$ $[\text{cis-Ru(bipy)}_2(\text{CO})\text{Cl}][\text{ClO}_4]$	$\text{NaBH}_4\text{-THF}$ $\text{NaBH}_4\text{-EtOH}$ $\text{NaBH}_4\text{-EtOH-PMcPh}_2$ $\text{NaBH}_4\text{-EtOH-PPh}_3$ $\text{NaBH}_4\text{-EtOH}$ $\text{NaBH}_4\text{-EtOH-PPh}_3$ $\text{NaBH}_4\text{-EtOH-P(OEt)}_3$ $\text{EtOH-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{-NaBH}_4$ $\text{NaBH}_4\text{-THF}$ $\text{NaBH}_4\text{-EtOH-P(OPh)}_3$ $\text{NaBH}_4\text{-EtOH-PPh}_3$ $\text{EtOH-Ph}_3\text{P-NaBH}_4$ $\text{EtOH-PPh}_3\text{-NaBH}_4$ $\text{EtOH-PPh}_3\text{-NaBH}_4$ $\text{NaBH}_4\text{-Et}_2\text{O-C}_6\text{H}_5\text{-EtOH}$ NaBH_4 $\text{H}_2\text{O-MeOH-NaBH}_4$ $\text{H}_2\text{O-MeOH-NaBH}_4$ $\text{H}_2\text{O-EtOH-NaBH}_4\text{-NH}_4\text{PF}_6$	$[\text{HOs}_8(\text{CO})_{18}]^-$ $\text{H}_6\text{W}(\text{PMc}_2\text{Ph})_3$ $\text{H}_4\text{Mo}(\text{PMcPh})_4$ $\text{H}_2\text{Mo}(\text{PPh}_3)_2\text{C}_6\text{H}_6\text{-h}^6$ $\text{H}_3\text{Re}(\text{PMc}_2\text{Ph})_3$ $\text{H}_4\text{Os}(\text{PPh}_3)_3$ $\text{H}_4\text{Ru}[\text{P}(\text{OEt})_3]_4$ $\text{HFeCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ $\text{h}^5\text{-C}_5\text{H}_5\text{Ru(PPh)}_3\text{H}$ $\text{CoH}[\text{P(OPh)}_3]_4$ $\text{CoH}_3(\text{PPh}_3)_3$ $\text{IrH}_3(\text{PPh}_3)_3$ (both isomers) $\text{Ir(PPh)}_3(\text{CO})\text{H}$ HRh(PPh)_4 $\text{trans-HNiCl[P(C}_6\text{H}_5)_3]_2$ $[\text{Pt}_2\text{Me}_2(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2][\text{PF}_6]$ $\text{HCo(DMGH)}_2 \cdot 2\text{PPh}_3^a$ $\text{HRh(DMGH)}_2\text{PPh}_3^a$ $[\text{cis-Ru(bipy)}_2(\text{CO})\text{H}][\text{PF}_6]$	18 19 20, 21 22 23 24 25 26 27 28-30 31 32 33 34 35 36 37, 38 39 40

^a DMGH = dimethylglyoximate monoanion.

loss of the volatile BH_3 and $[\text{HMo}_2(\text{CO})_{10}]^-$ formation⁴⁶. The reduction of $\text{Fe}[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]_2\text{Cl}_2$ with $[\text{BH}_4]^-$ affords a borohydride-containing species⁴⁷ that decomposes to $\text{Fe}[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_3]\text{H}_2$ on standing in THF.

Sodium borohydride can be used to synthesize reactive intermediates at low T, e.g., to prepare an unstable allyl hydride⁴⁸:

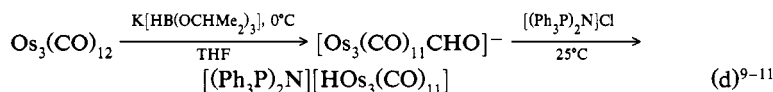
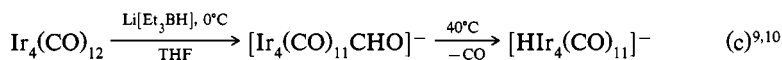
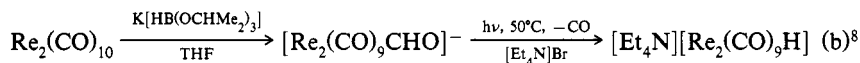
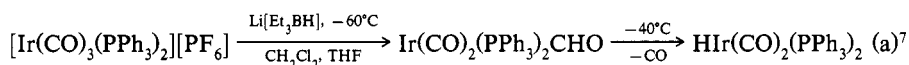


1. R. A. Schunn, in *Transition Metal Hydrides*, E. L. Muetterties, ed., Marcel Dekker, New York, 1971, p. 203.
2. H. D. Kaesz, R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
3. D. Giusto, *Inorg. Chim. Acta Rev.*, **6**, 91 (1972).
4. D. M. Roundhill, *Adv. Organomet. Chem.*, **13**, 273 (1975).
5. H. D. Kaesz, *Inorg. Synth.*, **17**, 52 (1977); a listing of all earlier preparations of transition-metal hydrides published in *Inorg. Synth.* as well as an introduction to newer preparations. Many of the preparations involve NaBH_4 .
6. A. P. Humphries, H. D. Kaesz, *Prog. Inorg. Chem.*, **25**, 145 (1979); a comprehensive review of all aspects of the chemistry of polynuclear hydrides.
7. G. L. Geoffroy, J. R. Lehman, *Adv. Inorg. Chem. Radiochem.*, **20**, 189 (1977).
8. M. L. H. Green, J. A. McCleverty, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).
9. R. B. King, *Organometallic Syntheses*, Vol. 1, Academic Press, New York, 1965.
10. M. L. H. Green, P. J. Knowles, *J. Chem. Soc., Perkin Trans. 1*, 989 (1973).
11. M. L. H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).
12. R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).
13. D. C. Harris, H. B. Gray, *J. Am. Chem. Soc.*, **97**, 3073 (1975).
14. M. R. Churchill, S. W.-Y. N. Chang, M. L. Berch, A. Davison, *J. Chem. Soc., Chem. Commun.*, 691 (1973).
15. D. K. Huggins, W. Fellmann, J. M. Smith, H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).
16. M. A. Andrews, S. W. Kirtley, H. D. Kaesz, *Inorg. Synth.*, **17**, 66 (1977).
17. H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).
18. C. R. Eady, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Chem. Commun.*, 302 (1976).
19. J. R. Moss, B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1910 (1972).
20. F. Pennella, *Inorg. Synth.*, **15**, 43 (1974).
21. P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 1467 (1973).
22. W. E. Silverthorn, *Inorg. Synth.*, **17**, 57 (1977).
23. P. G. Douglas, B. L. Shaw, *Inorg. Synth.*, **17**, 64 (1977).
24. N. Ahmad, J. J. Levison, S. D. Robinson, M. F. Uttley, *Inorg. Synth.*, **15**, 56 (1974).
25. W. G. Peet, D. H. Gerlach, *Inorg. Synth.*, **15**, 41 (1974).
26. P. Gianoccaro, A. Sacco, *Inorg. Synth.*, **17**, 69 (1977).
27. T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc., A*, 2376 (1971).
28. J. J. Levison, S. D. Robinson, *Inorg. Synth.*, **13**, 105 (1972).
29. D. Titus, A. A. Orio, H. B. Gray, *Inorg. Synth.*, **13**, 118 (1972).
30. E. L. Muetterties, F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 7920 (1974).
31. A. Sacco, M. Rossi, *Inorg. Synth.*, **12**, 19 (1970).
32. N. Ahmad, S. D. Robinson, M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 843 (1972).
33. G. Wilkinson, *Inorg. Synth.*, **13**, 126 (1972).
34. J. J. Levison, S. D. Robinson, *J. Chem. Soc., A*, 2947 (1970).
35. T. Saito, H. Munakata, H. Imoto, *Inorg. Synth.*, **17**, 84 (1977).
36. M. P. Brown, S. J. Cooper, A. A. Frew, L. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, M. A. Thompson, *J. Organomet. Chem.*, **198**, C33 (1980).
37. G. N. Schrauzer, R. J. Holland, *J. Am. Chem. Soc.*, **93**, 1505 (1971).
38. T.-H. Chao, J. H. Espenson, *J. Am. Chem. Soc.*, **100**, 129 (1978).
39. T. Ramasami, J. H. Espenson, *Inorg. Chem.*, **19**, 1846 (1980).

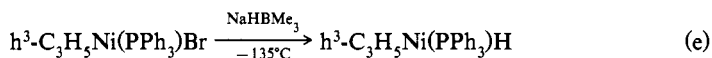
40. J. M. Kelly, J. G. Vos, *Angew. Chem., Int. Ed. Engl.*, 21, 628 (1982).
 41. C. R. Eady, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.*, 477 (1977).
 42. R. K. Nanda, M. G. H. Wallbridge, *Inorg. Chem.*, 3, 1798 (1964).
 43. B. D. James, R. K. Nanda, M. G. H. Wallbridge, *Inorg. Chem.*, 6, 1979 (1967).
 44. C. R. Lucas, *Inorg. Synth.*, 16, 109 (1976).
 45. R. J. Kinney, W. D. Jones, R. G. Bergman, *J. Am. Chem. Soc.*, 100, 7902 (1978).
 46. S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Gryniewicz, T. J. Marks, D. L. Tipton, B. R. Whittlesey, *J. Am. Chem. Soc.*, 99, 7154 (1977).
 47. M. V. Baker, L. D. Field, *J. Chem. Soc., Chem. Commun.*, 996 (1984).
 48. G. Carturan, A. Scrivanti, F. Morandini, *Angew. Chem., Int. Ed. Engl.*, 20, 112 (1981).

1.10.7.2. with Trialkylborohydride and Other Substituted Borohydrides.

Trialkylborohydride reducing agents differ from borohydride in their ability to transfer hydride directly to a carbonyl ligand without prior substitution in the coordination sphere. They are used to synthesize formyl complexes¹⁻⁵. When formyl complexes lose CO and undergo hydride migration from the formyl ligand to the metal, a transition-metal hydride results. The process is formally similar to nucleophilic attack by $[\text{OH}]^-$ on a carbonyl ligand, followed by loss of CO_2 and formation of a transition-metal hydride⁶. Examples of hydride syntheses via formyl complexes are:



However, formyl complexes undergo reactions other than decomposition to transition-metal hydrides^{5,7}; e.g., $\text{h}^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})(\text{CHO})$ disproportionates¹² to $\text{h}^5\text{-C}_5\text{H}_5\text{-(CO)(NO)ReCO}_2\text{CH}_2\text{Re}(\text{CO})(\text{NO})\text{C}_5\text{H}_5\text{-h}^5$. Thus, while trialkylborohydride reduction is the method of choice for formyl complexes and generates transition-metal anions for protonation to hydrides^{13,14}, it is not a general method for metal hydrides. Trialkylborohydride reduction generates an unstable allyl hydride at low T when no carbonyl ligands are present¹⁵:



Lithium triethylborohydride is more effective than NaBH_4 for preparing Mo and W tetrahydrides¹⁶, e.g.:



The yield is 70%, but it is only 4% from NaBH_4 .

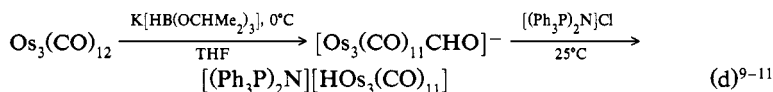
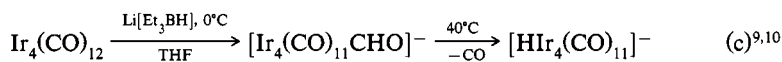
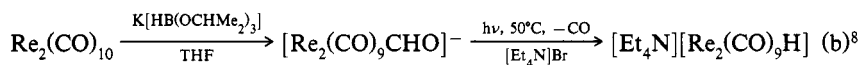
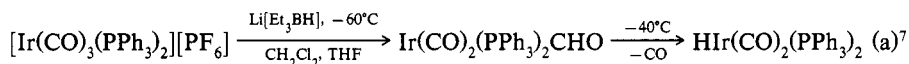
1.10. Formation of Bonds between Hydrogen and Transition Metals 223

1.10.7. by Reduction of Metal Complexes

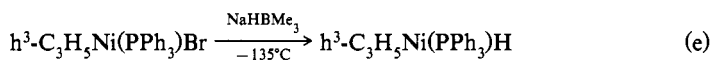
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47. M. V. Baker, L. D. Field, *J. Chem. Soc., Chem. Commun.*, 996 (1984).
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1.10.7.2. with Trialkylborohydride and Other Substituted Borohydrides.

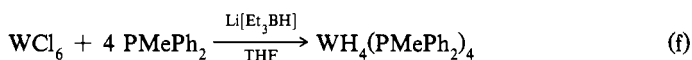
Trialkylborohydride reducing agents differ from borohydride in their ability to transfer hydride directly to a carbonyl ligand without prior substitution in the coordination sphere. They are used to synthesize formyl complexes¹⁻⁵. When formyl complexes lose CO and undergo hydride migration from the formyl ligand to the metal, a transition-metal hydride results. The process is formally similar to nucleophilic attack by [OH]⁻ on a carbonyl ligand, followed by loss of CO₂ and formation of a transition-metal hydride⁶. Examples of hydride syntheses via formyl complexes are:



However, formyl complexes undergo reactions other than decomposition to transition-metal hydrides^{5,7}; e.g., $\text{h}^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})(\text{CHO})$ disproportionates¹² to $\text{h}^5\text{-C}_5\text{H}_5\text{-(CO)(NO)ReCO}_2\text{CH}_2\text{Re}(\text{CO})(\text{NO})\text{C}_5\text{H}_5\text{-h}^5$. Thus, while trialkylborohydride reduction is the method of choice for formyl complexes and generates transition-metal anions for protonation to hydrides^{13,14}, it is not a general method for metal hydrides. Trialkylborohydride reduction generates an unstable allyl hydride at low T when no carbonyl ligands are present¹⁵:

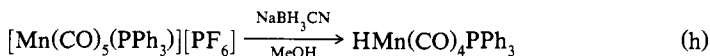
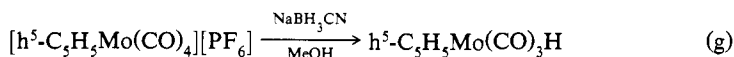


Lithium triethylborohydride is more effective than NaBH₄ for preparing Mo and W tetrahydrides¹⁶, e.g.:



The yield is 70%, but it is only 4% from NaBH₄.

Although cyanoborohydride ($[\text{BH}_3\text{CN}]^-$) is a selective reagent for ligand reductions^{17,18}, it also reduces some carbonyl cations to the corresponding hydrides in good yield¹⁸:



(J. R. NORTON)

1. C. P. Casey, S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976).
2. S. R. Winter, G. W. Cornett, E. W. Thompson, *J. Organomet. Chem.*, **133**, 339 (1977).
3. J. C. Selover, M. Marsi, D. W. Parker, J. A. Gladysz, *J. Organomet. Chem.*, **206**, 317 (1981).
4. K. P. Darst, C. M. Lukehart, *J. Organomet. Chem.*, **171**, 65 (1979).
5. J. A. Gladysz, *Adv. Organomet. Chem.*, **20**, 1 (1982).
6. H. D. Kaesz, *J. Organomet. Chem.*, **200**, 145 (1980).
7. W. Tam, G.-Y. Lin, J. A. Gladysz, *Organometallics*, **1**, 525 (1982).
8. C. P. Casey, S. M. Neumann, *J. Am. Chem. Soc.*, **100**, 2544 (1978).
9. R. L. Pruett, R. C. Schoening, J. L. Vidal, R. A. Fiato, *J. Organomet. Chem.*, **182**, C57 (1979).
10. R. C. Schoening, J. L. Vidal, R. A. Fiato, *J. Organomet. Chem.*, **206**, C43 (1981).
11. G. R. Steinmetz, E. D. Morrison, G. L. Geoffroy, *J. Am. Chem. Soc.*, **106**, 2559 (1984).
12. C. P. Casey, M. A. Andrews, D. R. McAlister, J. E. Rinz, *J. Am. Chem. Soc.*, **102**, 1927 (1980).
13. J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, J. C. Selover, *Inorg. Chem.*, **18**, 553 (1979).
14. J. A. Gladysz, W. Tam, G. M. Williams, D. L. Johnson, D. W. Parker, *Inorg. Chem.*, **18**, 1163 (1979).
15. H. Bönemann, *Angew. Chem., Int. Ed. Engl.*, **9**, 736 (1970).
16. R. H. Crabtree, G. G. Hlatky, *Inorg. Chem.*, **21**, 1273 (1982).
17. T. Bodnar, G. Coman, S. LaCroce, C. Lambert, K. Menard, A. Cutler, *J. Am. Chem. Soc.*, **103**, 2471 (1981).
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1.10.7.3. with Tetrahydroaluminate.

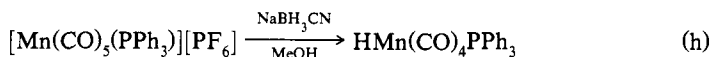
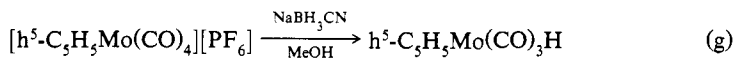
Lithium aluminum hydride is used almost as frequently as NaBH_4 (see §1.10.7.1), but even less is known about its mechanism of action, especially whether it reacts via an intermediate $[\text{AlH}_4]^-$ ligand. Complexes containing that ligand are known¹⁻⁴.

Examples of LiAlH_4 use are found in reviews⁵⁻¹⁰ and in¹¹⁻¹⁸ Table 1. Although LiAlH_4 is a more powerful reducing agent than NaBH_4 , the latter is used frequently in EtOH, while LiAlH_4 requires ether. Comparison of Table 1 with the corresponding table in §1.10.7.1 shows that transition-metal hydrides can be prepared by the use of either reagent.

(J. R. NORTON)

1. P. C. Wailes, H. Weigold, *J. Organomet. Chem.*, **24**, 405 (1970).
2. T. J. McNeese, S. S. Wreford, B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 500 (1978); a critical evaluation of claims of tetrahydroaluminate complexes.
3. G. S. Girolami, G. Wilkinson, M. Thornton-Pett, M. B. Hursthouse, *J. Am. Chem. Soc.*, **105**, 6752 (1983); earlier claims of $[\text{AlH}_4]^-$ complexes are listed.
4. E. B. Lovkovskii, G. L. Soloveichik, A. I. Sisov, B. M. Bulychev, A. I. Gusev, N. I. Kirillova, *J. Organomet. Chem.*, **265**, 167 (1984).

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3. J. C. Selover, M. Marsi, D. W. Parker, J. A. Gladysz, *J. Organomet. Chem.*, **206**, 317 (1981).
4. K. P. Darst, C. M. Lukehart, *J. Organomet. Chem.*, **171**, 65 (1979).
5. J. A. Gladysz, *Adv. Organomet. Chem.*, **20**, 1 (1982).
6. H. D. Kaesz, *J. Organomet. Chem.*, **200**, 145 (1980).
7. W. Tam, G.-Y. Lin, J. A. Gladysz, *Organometallics*, **1**, 525 (1982).
8. C. P. Casey, S. M. Neumann, *J. Am. Chem. Soc.*, **100**, 2544 (1978).
9. R. L. Pruett, R. C. Schoening, J. L. Vidal, R. A. Fiato, *J. Organomet. Chem.*, **182**, C57 (1979).
10. R. C. Schoening, J. L. Vidal, R. A. Fiato, *J. Organomet. Chem.*, **206**, C43 (1981).
11. G. R. Steinmetz, E. D. Morrison, G. L. Geoffroy, *J. Am. Chem. Soc.*, **106**, 2559 (1984).
12. C. P. Casey, M. A. Andrews, D. R. McAlister, J. E. Rinz, *J. Am. Chem. Soc.*, **102**, 1927 (1980).
13. J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, J. C. Selover, *Inorg. Chem.*, **18**, 553 (1979).
14. J. A. Gladysz, W. Tam, G. M. Williams, D. L. Johnson, D. W. Parker, *Inorg. Chem.*, **18**, 1163 (1979).
15. H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, **9**, 736 (1970).
16. R. H. Crabtree, G. G. Hlatky, *Inorg. Chem.*, **21**, 1273 (1982).
17. T. Bodnar, G. Coman, S. LaCroce, C. Lambert, K. Menard, A. Cutler, *J. Am. Chem. Soc.*, **103**, 2471 (1981).
18. T. Bodnar, E. Coman, K. Menard, A. Cutler, *Inorg. Chem.*, **21**, 1275 (1982).

1.10.7.3. with Tetrahydroaluminate.

Lithium aluminum hydride is used almost as frequently as NaBH_4 (see §1.10.7.1), but even less is known about its mechanism of action, especially whether it reacts via an intermediate $[\text{AlH}_4]^-$ ligand. Complexes containing that ligand are known¹⁻⁴.

Examples of LiAlH_4 use are found in reviews⁵⁻¹⁰ and in¹¹⁻¹⁸ Table 1. Although LiAlH_4 is a more powerful reducing agent than NaBH_4 , the latter is used frequently in EtOH, while LiAlH_4 requires ether. Comparison of Table 1 with the corresponding table in §1.10.7.1 shows that transition-metal hydrides can be prepared by the use of either reagent.

(J. R. NORTON)

1. P. C. Wailes, H. Weigold, *J. Organomet. Chem.*, **24**, 405 (1970).
2. T. J. McNeese, S. S. Wreford, B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 500 (1978); a critical evaluation of claims of tetrahydroaluminate complexes.
3. G. S. Girolami, G. Wilkinson, M. Thornton-Pett, M. B. Hursthouse, *J. Am. Chem. Soc.*, **105**, 6752 (1983); earlier claims of $[\text{AlH}_4]^-$ complexes are listed.
4. E. B. Lovkovskii, G. L. Soloveichik, A. I. Sisov, B. M. Bulychev, A. I. Gusev, N. I. Kirillova, *J. Organomet. Chem.*, **265**, 167 (1984).

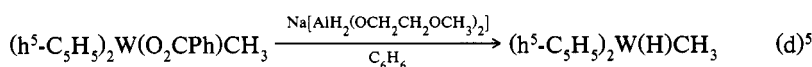
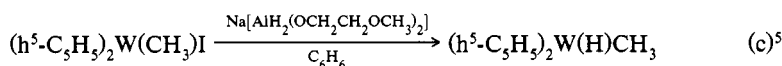
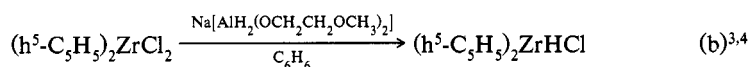
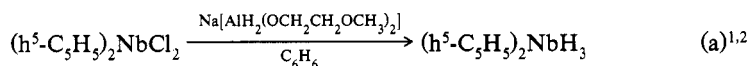
TABLE 1. PREPARATIONS OF TRANSITION-METAL HYDRIDES BY $[\text{AlH}_4]^-$ REACTIONS

Initial metal complex	Reagents	Product hydride	Refs.
TaCl_5	$\text{LiC}_3\text{H}_4\text{Me}-\text{THF}-\text{C}_6\text{H}_6-\text{LiAlH}_4$	$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TaH}_3$	11
$\text{WCl}_4(\text{PPh}_3)_2$	$\text{PPh}_3\text{Et}-\text{THF}-\text{LiAlH}_4$	$\text{H}_4\text{W}(\text{PPh}_3)_4$	12
$\text{WCl}_4(\text{PMe}_3)_3$	LiAlH_4	$\text{H}_5\text{W}(\text{PMe}_3)_3$	13
$\text{ReOCl}_3(\text{PPhEt})_2$	$\text{LiAlH}_4-\text{THF}$	$\text{H}_5\text{Re}(\text{PPhEt})_2$	7, 14, 15
$\text{ReCl}_3(\text{NPh})(\text{PMe}_3)_3$	LiAlH_4	$\text{HRe}(\text{NPh})(\text{PMe}_3)_2$	13
$\text{trans-ReCl}_3(\text{PPhEt})_3$	$\text{LiAlH}_4-\text{THF}$	$\text{H}_5\text{Re}(\text{PPhEt})_3$	7, 14, 15
$\text{FeCl}_2(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$	$\text{LiAlH}_4-\text{THF}$	$\text{HFeCl}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$	16
$[\text{Me}_3\text{PH}][\text{IrCl}_4(\text{PMe}_3)_2]$	$\text{LiAlH}_4-\text{THF}$	$\text{H}_3\text{Ir}(\text{PMe}_3)_2$	15, 17
$\text{CuCl}(\text{PPh}_3)_3$	$\text{LiAlH}_4-\text{Et}_2\text{O}$	HCuPPh_3	18

5. R. A. Schunn, in *Transition Metal Hydrides*, E. L. Muetterties, ed., Marcel Dekker, New York, 1971, p. 203.
6. H. D. Kaesz, R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
7. D. Giusto, *Inorg. Chim. Acta Rev.*, **6**, 91 (1972).
8. H. D. Kaesz, in *Inorg. Synth.*, **17**, 52 (1977); a listing of all earlier preparations of transition-metal hydrides published in *Inorg. Synth.* as well as an introduction to newer preparations.
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11. U. Klabunde, G. W. Parshall, *J. Am. Chem. Soc.*, **94**, 9081 (1972).
12. P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 1467 (1973).
13. M. B. Hursthouse, D. Lyons, M. Thornton-Pett, G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 476 (1983).
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15. R. Bau, W. E. Carroll, D. W. Hart, R. G. Teller, T. F. Koetzle, in *Transition Metal Hydrides*, R. Bau, ed., American Chemical Society, Advances in Chemistry Series No. 167, Washington, DC, 1978, p. 73.
16. M. J. Mays, B. E. Prater, *Inorg. Synth.*, **15**, 23 (1974).
17. E. K. Barefield, *Inorg. Synth.*, **15**, 36 (1974).
18. R. D. Stephens, *Inorg. Synth.*, **19**, 87 (1979).

1.10.7.4. with Alkoxyaluminum Hydrides.

The solubility of $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ in aromatic hydrocarbons makes it unique among the main-group hydride reagents used to form transition-metal hydrogen bonds. It is the reagent of choice for:



1.10. Formation of Bonds between Hydrogen and Transition Metals 225

1.10.7. by Reduction of Metal Complexes

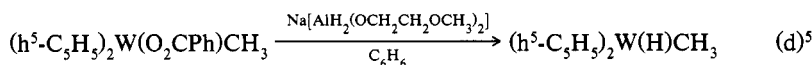
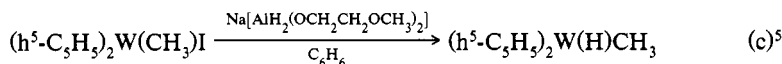
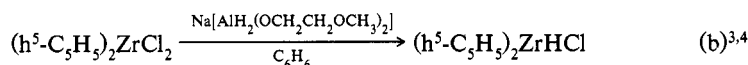
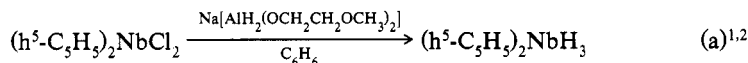
TABLE 1. PREPARATIONS OF TRANSITION-METAL HYDRIDES BY $[\text{AlH}_4]^-$ REACTIONS

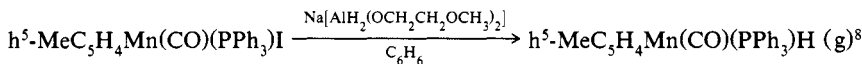
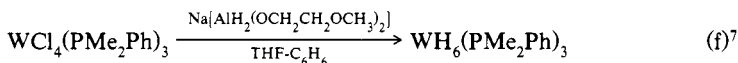
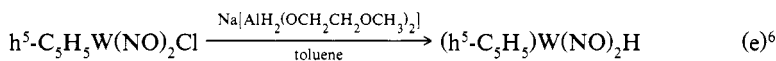
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$\text{WCl}_4(\text{PPh}_3\text{Et})_2$	$\text{PPh}_3\text{Et}-\text{THF}-\text{LiAlH}_4$	$\text{H}_2\text{W}(\text{PPh}_3\text{Et})_4$	12
$\text{WCl}_4(\text{PMe}_3)_3$	LiAlH_4	$\text{H}_2\text{W}(\text{PMe}_3)_3$	13
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$\text{trans-ReCl}_3(\text{PPhEt})_3$	$\text{LiAlH}_4-\text{THF}$	$\text{H}_2\text{Re}(\text{PPhEt})_3$	7, 14, 15
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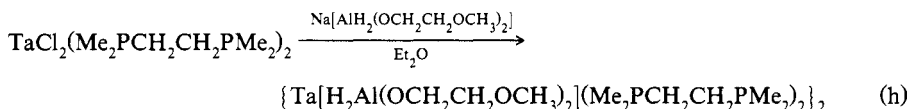
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One such reaction results in the isolation of a stable aluminohydride complex⁹:



(J. R. NORTON)

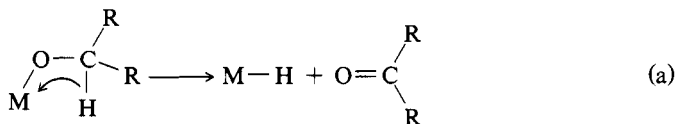
1. J. A. Labinger, in *Transition Metal Hydrides*, R. Bau, ed., American Chemical Society, Advances in Chemistry Series No. 167, Washington, DC, 1978, p. 149.
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4. D. B. Carr, J. Schwartz, *J. Am. Chem. Soc.*, **101**, 3521 (1979).
5. N. J. Cooper, M. L. H. Green, R. Mahtab, *J. Chem. Soc., Dalton Trans.*, 1557 (1979).
6. P. Legzdins, D. T. Martin, *Inorg. Chem.*, **18**, 1250 (1979).
7. R. H. Crabtree, G. G. Hlatky, *Inorg. Chem.*, **23**, 2388 (1984).
8. B. W. Hames, P. Legzdins, J. C. Oxley, *Inorg. Chem.*, **19**, 1565 (1980).
9. T. J. McNeese, S. S. Wreford, B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 500 (1978).

1.10.8. by Hydrogen Transfer to the Metal

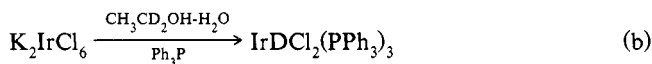
1.10.8.1. from Alcohols in Basic Media.

This method, most frequently employing EtOH, is used widely because the reaction is easy to perform. Examples are found in reviews¹⁻⁵ and in⁶⁻¹⁷ Table 1.

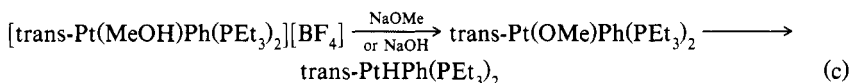
β -Hydrogen is eliminated from a coordinated alkoxide ligand:



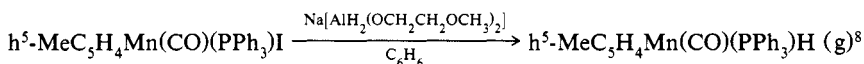
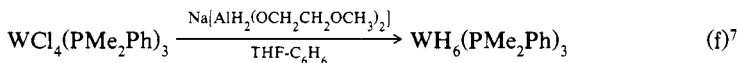
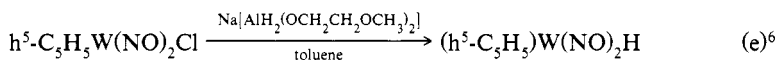
as is implied by the incorporation of a deuterium label¹⁸:



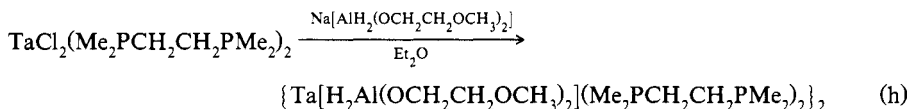
and proved by observation of an intermediate methoxy complex¹⁹:



226 1.10. Formation of Bonds between Hydrogen and Transition Metals



One such reaction results in the isolation of a stable aluminohydride complex⁹:



(J. R. NORTON)

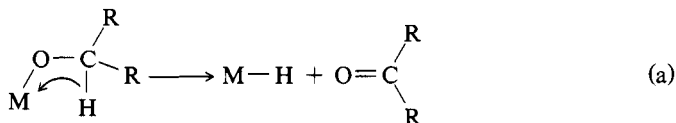
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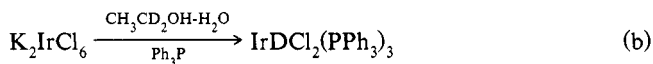
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β -Hydrogen is eliminated from a coordinated alkoxide ligand:



as is implied by the incorporation of a deuterium label¹⁸:



and proved by observation of an intermediate methoxy complex¹⁹:

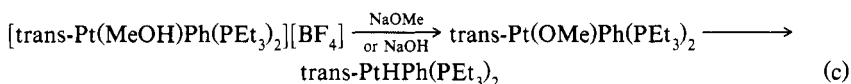
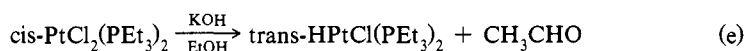
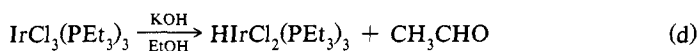


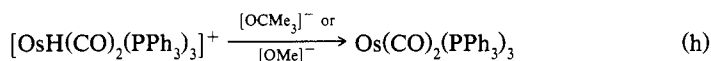
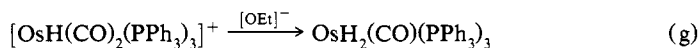
TABLE 1. PREPARATION OF TRANSITION-METAL HYDRIDES FROM ALCOHOLS

Initial metal complex	Reagents	Hydride	Refs.
$\text{RuCl}_3 \cdot x \text{H}_2\text{O}$	$\text{PPh}_3\text{-HCHO-KOH-EtOH}$	$\text{H}_2\text{Ru}(\text{CO})(\text{PPh}_3)_3$	6, 7
$\text{Na}_2\text{OsCl}_6 \cdot 6 \text{H}_2\text{O}$	$\text{PPh}_3\text{-HCHO-MeOCH}_2\text{-CH}_2\text{OH}$	$\text{HOsCl}(\text{CO})(\text{PPh}_3)_3$	6, 7
$\text{RhCl}_3 \cdot x \text{H}_2\text{O}$	$\text{PPh}_3\text{-KOH-EtOH}$	$\text{HRh}(\text{PPh}_3)_4$	6, 7
$\text{Na}_2\text{IrCl}_6 \cdot 6 \text{H}_2\text{O}$	$\text{PPh}_3\text{-HCHO-KOH-MeOCH}_2\text{CH}_2\text{OH}$	$\text{HIr}(\text{CO})(\text{PPh}_3)_3$	6
$\text{Ru}(\text{NO})\text{Cl}_3$	$\text{PPh}_3\text{-KOH-EtOH}$	$\text{HRu}(\text{NO})(\text{PPh}_3)_3$	8
$\text{RuCl}_2(\text{PPh}_3)_3$	NaOAc-MeOH	$\text{HRu}(\text{OAc})(\text{PPh}_3)_3$	9
$[\text{Ru}_2\text{Cl}_2(\text{PEt}_2\text{Ph})_6]\text{Cl}$	KOH-EtOH	$\text{HRuCl}(\text{CO})(\text{PEt}_2\text{Ph})_3$	10
$\text{cis-RuClMe}(\text{PMe}_3)_4$	NaOMe-THF	$\text{cis-HRuMe}(\text{PMe}_3)_4$	11
$\text{RhCl}_3 \cdot x \text{H}_2\text{O}$	EtOH-PEtPh_2	$\text{HRhCl}_2(\text{PEtPh}_2)_3$	12, 13
$\text{H}_2[\text{IrCl}_6]$	EtOH-COD	$[\text{HIrCl}_2(\text{C}_8\text{H}_{12})_2]$	14
$[\text{Ir}(\text{COD})\text{Cl}]_2$	$\text{EtOH-PEt}_2\text{Ph-NaBPh}_4$	$[\text{H}_2\text{Ir}(\text{PEt}_2\text{Ph})_4][\text{BPh}_4]$	15
$[\text{cis-Os}(\text{bipy})_2(\text{CO})\text{Cl}][\text{PF}_6]$	$\text{PPh}_3\text{-HO}(\text{CH}_2)_2\text{OH}$	$[\text{cis-Os}(\text{bipy})_2(\text{CO})\text{H}][\text{PF}_6]$	16
$[\text{cis-Ir}(\text{bipy})_2(\text{OSO}_2\text{CF}_3)_2][\text{CF}_3\text{SO}_3]$	$\text{PPh}_3\text{-HO}(\text{CH}_2)_2\text{OH}$	$[\text{cis-Ir}(\text{bipy})_2(\text{PPh}_3)\text{H}][\text{PF}_6]$	17

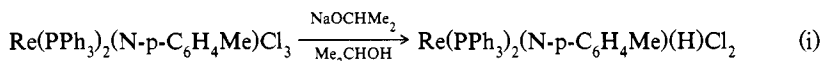
In favorable cases like Eq. (b), the addition of strong base is not required; either a weak base, such as PPh_3 , can deprotonate sufficient alcohol to enable the reaction to proceed, or β -hydrogen elimination can occur even when the alcohol instead of the alkoxide is coordinated. The organic product is the aldehyde or ketone (confirmed in only a few cases)^{2,20,21}:



The alkoxide of a tertiary alcohol cannot generate a hydride by this mechanism. The importance of the type of alcohol employed is illustrated by the contrast between Eqs. (g) and (h)²²:

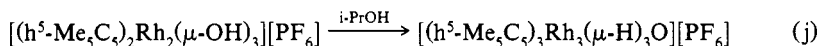


Whereas treatment with ethoxide generates another hydride ligand, treatment with *t*-butoxide results in deprotonation. Similarly, whereas treatment of $\text{Re}(\text{PPh}_3)_2\text{-(NC}_6\text{H}_4\text{Me)Cl}_3$ with isopropoxide generates a hydride ligand:



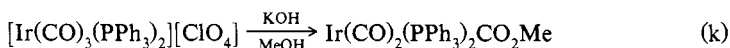
t-butoxide gives no reaction²³ at 100°C in *t*-BuOH.

As Eq. (h) illustrates, $[\text{MeO}]^-$ can fail to generate a hydride ligand; a stable methoxo complex is formed²³ when MeOH is used in Eq. (i). Complications may occur with other primary alcohols as well; EtOH, n-PrOH and n-BuOH are oxidized to carboxylato bridges²⁴ when substituted for i-PrOH, e.g.:



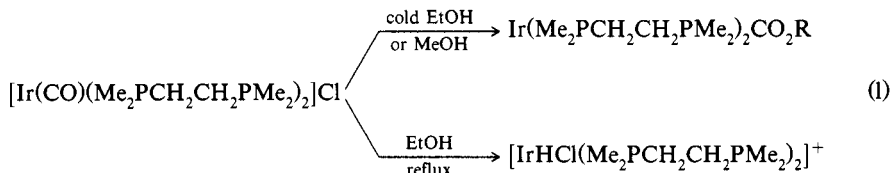
In contrast, sec-BuOH gives satisfactory results.

Reaction (h) illustrates a limitation of the use of alkoxides for generating hydride ligands. A vacant coordination site must be generated so that the alcohol or alkoxide ion can attack the metal rather than any ligand [such as the hydrogen ligand in Eq. (h) or the carbonyl ligand in Eq. (k)²⁵] subject to nucleophilic attack:



Carbonyl ligands with high $\nu(\text{C}=\text{O})$ stretching frequencies are particularly susceptible to attack²⁶.

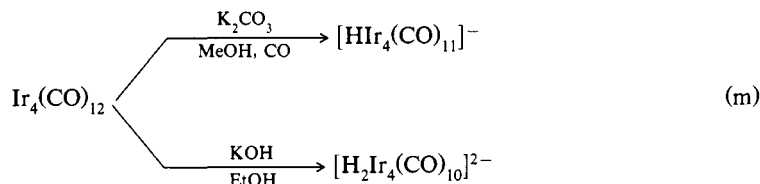
Sometimes either attack on the metal (leading to hydride formation) or attack on a carbonyl group can occur, depending on reaction conditions²⁷:



The formation of a carboalkoxy ligand, although kinetically favored, is reversible, whereas ligand dissociation and hydride formation are irreversible.

When side reactions do not interfere, the use of alcohol and base conveniently yields metal hydride. Each of the first four reactions in Table 1 prepares a complex transition-metal hydride from a metal salt in a few minutes, but only with triphenylphosphine.

The formaldehyde in some of these reactions is not only the source of the carbonyl ligands, but is also a potential alternative to the alcohol solvent as source of the hydride ligands. A similar ambiguity exists in the many hydride preparations in which H_2O and $[\text{OH}]^-$ are present as well as ROH and $[\text{RO}]^-$, e.g., in^{28,29}:



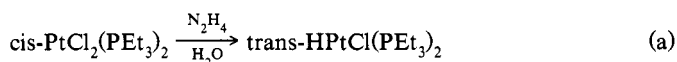
the hydrides may arise from $[\text{OH}]^-$ attack on carbonyl ligands (see §1.10.9), rather than from coordinated alkoxide.

(J. R. NORTON)

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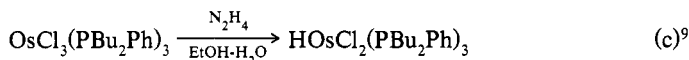
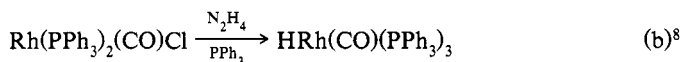
1.10.8.2. from Hydrazine.

Although one of the first discovered¹ for transition-metal hydrogen bonds, this method is now seldom used². It gives the (Et₃P)₂Pt hydrido-chloride in excellent yield^{3,4}:



but it forms Pt(0) complexes when other phosphines are present⁵. Isolation of an intermediate mixture of [Pt(PPh₃)₂(μ-N₂H)]₂²⁺ and [Pt(PPh₃)₂(μ-NH₂)]₂²⁺ is claimed^{6,7}.

Hydrazine is also successfully employed in:



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1.10. Formation of Bonds between Hydrogen and Transition Metals 229

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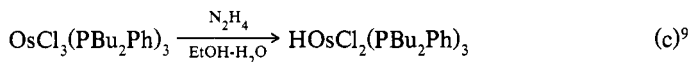
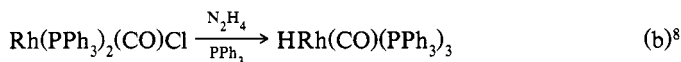
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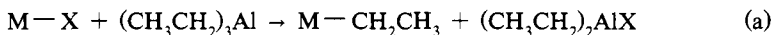
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1.10.8.3. from Aluminum Alkyls.

Aluminum alkyls, although inconvenient to handle because of their spontaneous inflammability, are powerful reducing agents and are applied to the synthesis of transition-metal hydrides^{1,2}. They, and the organomagnesium halide reagents to be discussed in §1.10.8.4, function by initial alkylation of the transition metal (e.g., for Et₃Al):

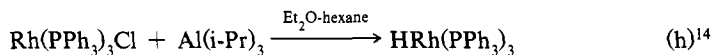
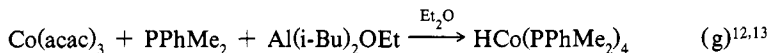
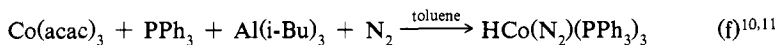
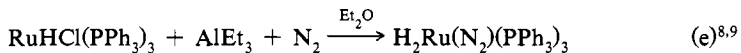
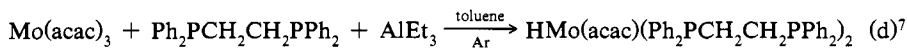
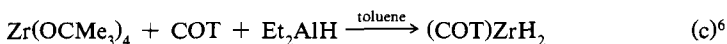


followed by formation of a hydride ligand by β -hydrogen elimination:



Reaction (a) requires that the metal be less electropositive than Al—a requirement met by most transition elements. Reaction (b) requires that a vacant coordination site be available (the olefin produced by β -hydrogen elimination must be at least transiently coordinated³), and that the alkyl group possess at least one β -hydrogen^{4,5}.

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(J. R. NORTON)

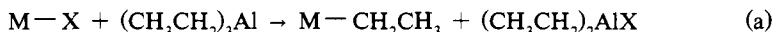
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230 1.10. Formation of Bonds between Hydrogen and Transition Metals
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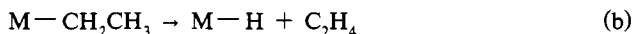
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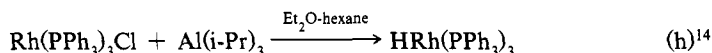
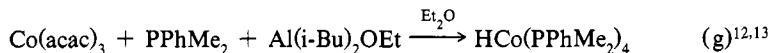
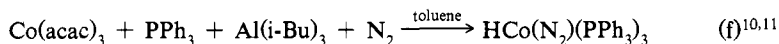
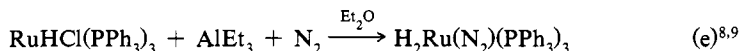
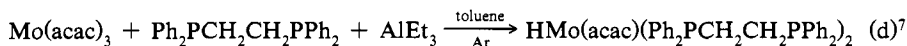
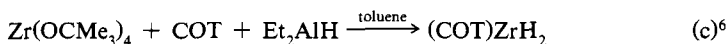


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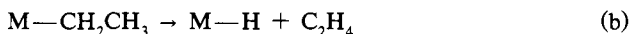
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1.10.8.4. from Alkylmagnesium Halides.

Although their use is becoming less common, organomagnesium halide reagents convert metal halides into hydrides¹⁻³. Like the Al alkyls discussed in §1.10.8.3, organomagnesium halide reagents function by initial alkylation of the transition metal [e.g., in Eq. (a) for EtMgBr]:

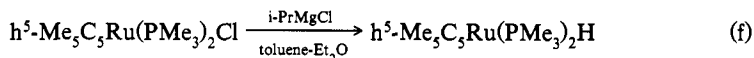
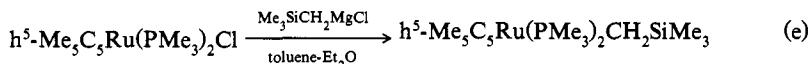
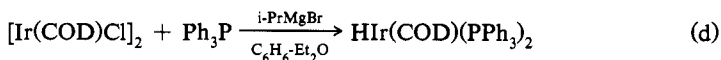
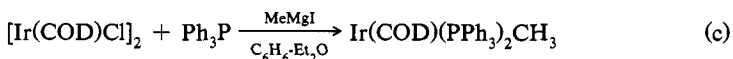


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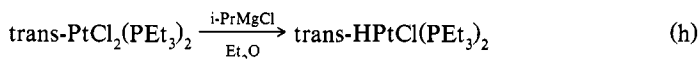
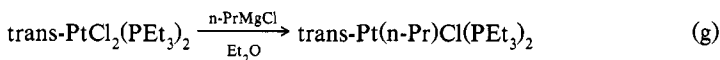


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Isopropylmagnesium halide reagents, therefore, are effective at forming transition-metal hydrides; methyl, phenyl and other magnesium halide reagents without β -hydrogens give the corresponding organometallic complexes^{7,8}:



Even an *n*-propylmagnesium halide reagent forms a hydride less readily than the corresponding isopropyl reagent, cf.⁸:



1.10. Formation of Bonds between Hydrogen and Transition Metals 231

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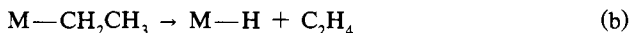
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Although their use is becoming less common, organomagnesium halide reagents convert metal halides into hydrides¹⁻³. Like the Al alkyls discussed in §1.10.8.3, organomagnesium halide reagents function by initial alkylation of the transition metal [e.g., in Eq. (a) for EtMgBr]:

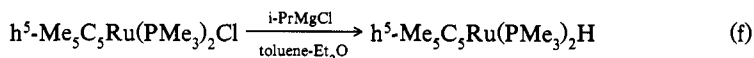
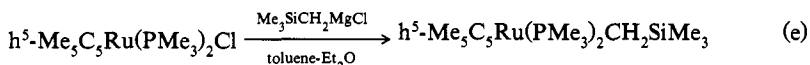
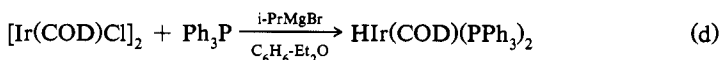
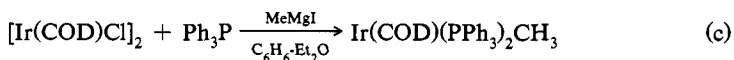


followed by formation of a hydride ligand by β -hydrogen elimination:

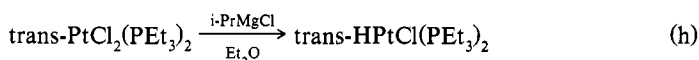
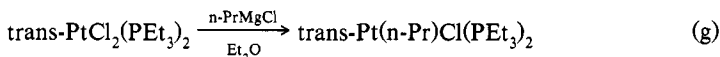


Reaction (a) requires that the metal be less electropositive than Mg—a requirement met by most transition elements. Reaction (b) requires that a vacant coordination site be available (the olefin produced by β -hydrogen elimination must be at least transiently coordinated⁴), and that the alkyl group possess at least one β -hydrogen. Such eliminations are easier for secondary and tertiary alkyl ligands than for the more stable primary ones^{5,6}.

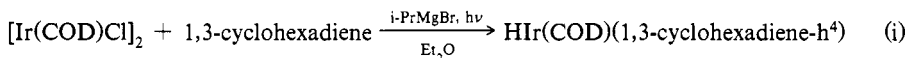
Isopropylmagnesium halide reagents, therefore, are effective at forming transition-metal hydrides; methyl, phenyl and other magnesium halide reagents without β -hydrogens give the corresponding organometallic complexes^{7,8}:



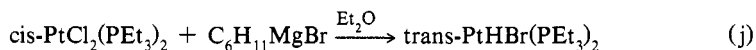
Even an *n*-propylmagnesium halide reagent forms a hydride less readily than the corresponding isopropyl reagent, cf.⁸:



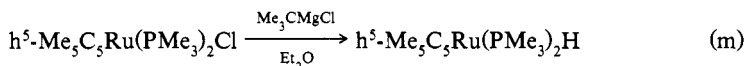
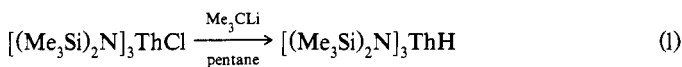
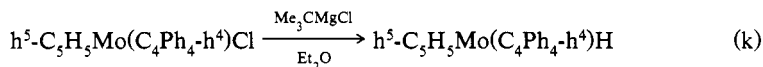
Another example [related to Eq. (d)] of the use of an isopropylmagnesium halide for the synthesis of a transition-metal hydride is^{10,11}:



As a secondary organomagnesium halide reagent, cyclohexylmagnesium bromide may also be useful for the synthesis of metal hydrides^{8,14,15}:



but over half of the hydride ligand arises from hydrolysis instead of from β -hydrogen elimination^{3,13}. Tertiary organomagnesium halide reagents or other tertiary organometallics may be more effective for hydride synthesis^{8,14,15}:



Organomagnesium halide reagents and organolithiums attack carbonyl ligands, particularly when the latter have high $\nu(\text{C}=\text{O})$ stretching frequencies and are susceptible to nucleophilic attack^{16,17}. These organometallic reagents are, therefore, best used with complexes that do not contain carbonyls.

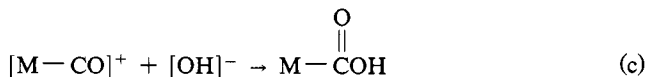
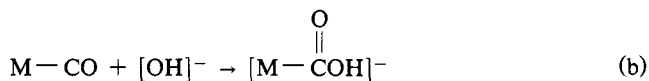
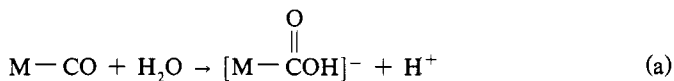
(J. R. NORTON)

1. R. A. Schunn, in *Transition Metal Hydrides*, E. L. Muetterties, ed., Marcel Dekker, New York, 1971, p. 203.
2. H. D. Kaesz, R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
3. D. M. Roundhill, *Adv. Organomet. Chem.*, **13**, 273 (1975).
4. D. E. Reger, E. C. Culbertson, *J. Am. Chem. Soc.*, **98**, 2789 (1976).
5. P. J. Davidson, M. F. Lappert, R. Pearce, *Chem. Rev.*, **76**, 219 (1976); an excellent review, including references to earlier reviews of decomposition mechanisms for σ -bonded organotransition-metal complexes.
6. R. R. Schrock, G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976); a review of early transition-metal alkyls and their decomposition mechanisms, including β -hydrogen elimination.
7. H. Yamazaki, M. Takesada, N. Hagihara, *Bull. Chem. Soc. Jpn.*, **42**, 275 (1969).
8. T. D. Tilley, R. H. Grubbs, J. E. Bercaw, *Organometallics*, **3**, 274 (1984).
9. J. Chatt, R. S. Coffey, A. Gough, D. T. Thompson, *J. Chem. Soc.*, **A**, 190 (1968).
10. J. Müller, H. Menig, P. V. Rinze, *J. Organomet. Chem.*, **181**, 387 (1979).
11. J. Müller, H. Mehnig, J. Pickardt, *Angew. Chem., Int. Ed. Engl.*, **20**, 401 (1981).
12. J. Chatt, B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).
13. R. J. Cross, F. Glockling, *J. Organomet. Chem.*, **3**, 253 (1964).
14. R. B. King, A. Efraty, *J. Chem. Soc., Chem. Commun.*, 1370 (1970).
15. H. W. Turner, S. J. Simpson, R. A. Andersen, *J. Am. Chem. Soc.*, **101**, 2782 (1979).
16. D. J. Darensbourg, M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).
17. M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, C. Hasday, *J. Am. Chem. Soc.*, **95**, 5919 (1973).

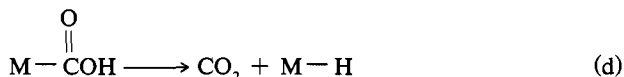
- 1.10. Formation of Bonds between Hydrogen and Transition Metals 233
 1.10.9. by Decarboxylation of Hydroxycarbonyl or Formate Complexes.

1.10.9. by Decarboxylation of Hydroxycarbonyl or Formate Complexes.

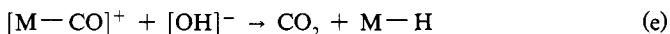
Hydride synthesis by metal-carbonyl hydrolysis is used widely, and mechanistic details are emerging. The reaction begins with nucleophilic attack by H_2O or $[\text{OH}]^-$ on a carbonyl ligand:



The loss of CO_2 in some form leaves a metal hydride:



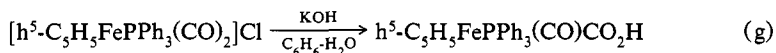
Overall, the reaction converts a cationic carbonyl to a neutral hydride:



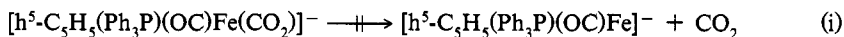
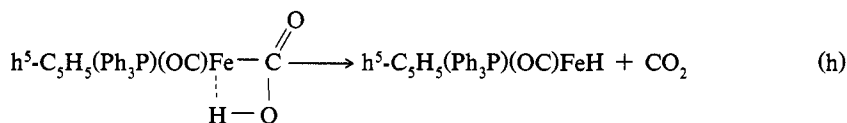
or a neutral carbonyl to an anionic hydride:



Several hydroxycarbonyl are isolable and convertible to hydrides^{1,2}. The product of reaction (g) is stable when extracted into benzene immediately after formation³:

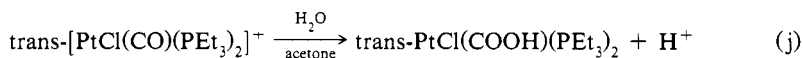


It is amphoteric, being deprotonated by xs KOH while dissociating hydroxyl ion [i.e., reversing Eq. (g)] in solvents of high dielectric constant such as formamide. The neutral hydroxycarbonyl complex loses CO_2 on warming, whereas its potassium salt is stable in solution even at 100°C :

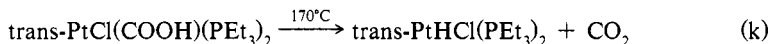


Concerted elimination of CO_2 is, therefore, faster than decarboxylation of the anion, perhaps because of the high energy of the basic anion that would be generated if reaction (i) occurred³.

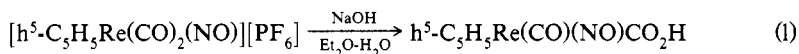
Similarly, treatment of $\text{trans-[PtCl(CO)(PEt}_3)_2]^+$ in acetone with H_2O gives a hydroxycarbonyl complex; the addition of HClO_4 reverses the process:



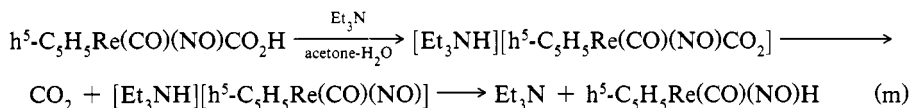
The solid hydroxycarbonyl complex loses CO_2 only slowly^{2,4}:



A different conclusion of the decarboxylation step is offered^{5,6} by $\text{h}^5\text{-C}_5\text{H}_5\text{-Re(CO)(NO)CO}_2\text{H}$:



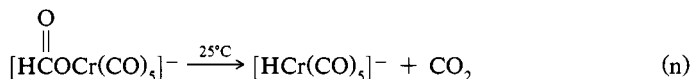
Although this hydroxycarbonyl complex is stable as a solid to 100°C , treatment with catalytic Et_3N or other bases⁶ causes decarboxylation to the hydride:



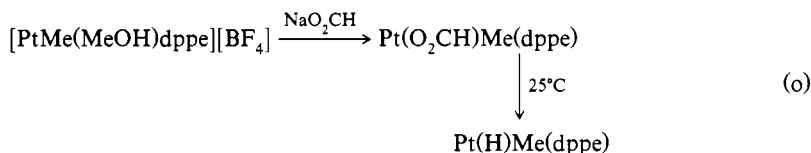
Treatment of $[\text{h}^5\text{-C}_5\text{H}_5\text{Re(CO)}_2(\text{NO})]^+$ with aq Et_3N is the standard method for preparing^{5,6} $\text{h}^5\text{-C}_5\text{H}_5\text{Re(CO)(NO)H}$.

The stability of $\text{h}^5\text{-C}_5\text{H}_5\text{Re(CO)(NO)CO}_2\text{H}$ arises from its high barrier to CO dissociation, whereas PPh_3 dissociation in $\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)(PPh}_3\text{)CO}_2\text{H}$ is facile and provides a vacant coordination site as required for decarboxylation. The ease of hydroxycarbonyl complex decarboxylation varies greatly^{7,8}.

Hydride complexes also are available from the decarboxylation of complexes containing formate, an isomer of the hydroxycarbonyl ligand⁹⁻¹¹:



However, formate and hydroxycarbonyl complexes do not interconvert intramolecularly¹⁰; therefore, neither species is an intermediate in the decarboxylation of the other. Formate ion is useful for the generation¹² of thermally unstable hydrides at low T:



The chiral complex $\text{h}^5\text{-C}_5\text{H}_5\text{Re(NO)(PPh}_3\text{)O}_2\text{CH}$ decarboxylates¹² to $\text{h}^5\text{-C}_5\text{H}_5\text{Re(NO)-(PPh}_3\text{)H}$ without PPh_3 dissociation and with retention at Re.

The synthetic limitations of metal-carbonyl hydrolysis arise from the requirement for initial nucleophilic attack on a carbonyl ligand. The susceptibility of carbonyl to such attack varies inversely with the extent to which it is serving as a π acceptor and can be predicted from its IR carbonyl stretching frequency and force constant^{14,15}. Whereas some electron-poor cationic carbonyls can be attacked by H_2O , as in Eq. (j),

neutral carbonyls require $[\text{OH}]^-$; for electron-rich carbonyls with CO stretching frequencies lowered by substantial π backbonding, strongly basic conditions may be required (see Table 1). The more nucleophilic NaSH [which leads to COS elimination after formation of an $\text{MC}(\text{O})\text{SH}$ intermediate] often gives²³ better results than NaOH:

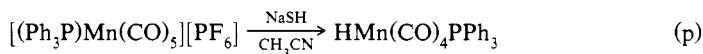


TABLE 1. FORMATION OF HYDRIDES BY BASE HYDROLYSIS OF METAL-CARBONYL COMPLEXES

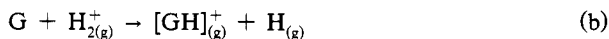
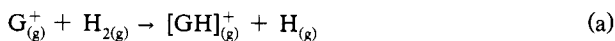
Carbonyl complex	Base and conditions	Product	Refs.
$\text{Cr}(\text{CO})_6$	$\text{KOH}-\text{H}_2\text{O}-\text{MeOH}-\text{THF}$, 50°C	$\text{K}[\text{HCr}_2(\text{CO})_{10}]$	16
$\text{Fe}(\text{CO})_5$	$\text{NaOH}-\text{H}_2\text{O}-\text{MeOH}-[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$	$[(\text{Ph}_3\text{P})_2\text{N}][\text{HFe}(\text{CO})_4]$	17
$\text{Ru}_3(\text{CO})_{12}$	H_2O , 135°C	$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	18
$[\text{Mn}(\text{CO})_6][\text{BF}_4]$	$\text{H}_2\text{O}-\text{CH}_3\text{CN}$	$\text{HMn}(\text{CO})_5$	19, 20
$[\text{PtCl}(\text{CO})(\text{PEt}_3)_2][\text{BF}_4]$	$\text{H}_2\text{O}-\text{MeOH}$, 110°C	$\text{PtHCl}(\text{PEt}_3)_2$	21, 22

(J. R. NORTON)

1. D. J. Darensbourg, *Isr. J. Chem.*, **15**, 247 (1977).
2. J. Halpern, *Comments Inorg. Chem.*, **1**, 3 (1981).
3. N. Grice, S. C. Kao, R. Petit, *J. Am. Chem. Soc.*, **101**, 1627 (1979); includes a brief but comprehensive historical survey with refs. to proposed MCO_2H intermediates.
4. M. Catellani, J. Halpern, *Inorg. Chem.*, **19**, 566 (1980); includes an excellent survey of MCO_2H complexes postulated as intermediates.
5. C. P. Casey, M. A. Andrews, J. E. Rinz, *J. Am. Chem. Soc.*, **101**, 741 (1979).
6. J. R. Sweet, W. A. G. Graham, *Organometallics*, **1**, 982 (1982).
7. W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, V. K. Wang, J. A. Gladysz, *J. Am. Chem. Soc.*, **104**, 141 (1982).
8. D. H. Gibson, K. Owens, T.-S. Ong, *J. Am. Chem. Soc.*, **106**, 1125 (1984).
9. D. J. Darensbourg, R. A. Kudarowski, *Adv. Organomet. Chem.*, **22**, 129 (1983).
10. D. J. Darensbourg, A. Rokicki, *Organometallics*, **1**, 1685 (1982).
11. J. V. Caspar, B. P. Sullivan, T. J. Meyer, *Organometallics*, **2**, 551 (1983).
12. D. P. Arnold, M. A. Bennett, *J. Organomet. Chem.*, **199**, C17 (1980).
13. J. H. Merrifield, J. A. Gladysz, *Organometallics*, **2**, 782 (1983).
14. D. J. Darensbourg, M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).
15. D. J. Darensbourg, B. J. Baldwin, J. A. Froelich, *J. Am. Chem. Soc.*, **102**, 4688 (1980).
16. M. D. Grillone, B. B. Kedzia, *J. Organomet. Chem.*, **140**, 161 (1977).
17. M. Y. Darensbourg, D. J. Darensbourg, H. L. C. Barros, *Inorg. Chem.*, **17**, 297 (1978).
18. J. A. Froelich, D. J. Darensbourg, *Inorg. Chem.*, **16**, 960 (1977).
19. C. R. Eady, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.*, 838 (1977).
20. W. Hieber, T. Kruck, *Z. Naturforsch., Teil B*, **16**, 709 (1961).
21. D. J. Darensbourg, J. A. Froelich, *J. Am. Chem. Soc.*, **99**, 4726 (1977).
22. H. C. Clark, K. R. Dixon, W. J. Jacobs, *J. Am. Chem. Soc.*, **91**, 1346 (1967).
23. H. C. Clark, W. J. Jacobs, *Inorg. Chem.*, **9**, 1229 (1970).

1.11. Formation of Bonds between Hydrogen and Elements of Group 0

There are no compounds that contain hydrogen-group 0 element (G) bonds. The cations $[\text{GH}]^+$ however, are generated in ion-molecule reactions¹:



The proton affinities [i.e., $-\Delta H$ for $\text{G}_{(\text{g})} + \text{H}_{(\text{g})}^+$] from such studies are listed in Table 1. As may be appreciated from the thermochemical cycle below, the electron affinity of $[\text{GH}]_{(\text{g})}^+$ is equal to the electron affinity of the proton (+13.6 eV) less the proton affinity of G, if $\Delta H [\text{GH}_{(\text{g})} \rightarrow \text{G}_{(\text{g})} + \text{H}_{(\text{g})}]$ is zero. Because the last condition is likely to be approximately true for all of the gases, the electron affinities of the $[\text{GH}]^+$ cations decrease down the series, and $E[\text{XeH}]^+ \leq +7.6$ eV. Thus hydrox Xenonium salts may be preparable. To stabilize $[\text{GH}]^+$ in a salt, $[\text{GH}]^+\text{X}_{(\text{s})}^-$, it is essential to have a combined lattice energy and electron affinity for X that exceeds the electron affinity of $[\text{GH}]^+$, otherwise the electron will simply transfer from X^- to $[\text{GH}]^+$. The problem of the generation of G—H bonds in cations $[\text{GH}]^+$ is to find an anion X^- that fulfills not only those conditions but also does not abstract the proton from the cation:

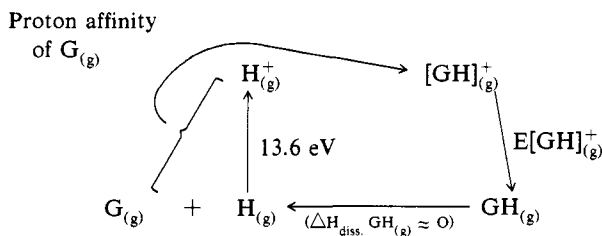


TABLE 1. PROTON AFFINITIES (PA) OF NOBLE GASES^a

	He	Ne	Ar	Kr	Xe
PA (g) (eV)	1.8	2.2	3.0	≥ 4	≥ 6

^a From Ref. 1.

(N. BARTLETT)

1. G. von Büнау, *Fortschr. Chem. Forsch.*, 5, 374 (1965).

1.12. Reversible Formation of Metal Hydrides by Direct Reaction of Hydrogen

1.12.1. Introduction

This chapter deals with metal–hydrogen compounds formed directly from metal and H_2 :



where M may be a group IA–VIII metal (including lanthanide or actinide), alloy or intermetallic compound. The reaction is spontaneous, exothermic and easily reversible.

Although many metals dissolve large amounts of hydrogen to form solid solutions, the hydride, MH_x shown in Eq. (a) refers only to a new phase, different from the hydrogen-saturated metal. The definite hydride phase may be detected either by a change in crystal structure, by discontinuous change in lattice parameters on hydride formation or by thermodynamic data indicating new phase formation. The latter technique is illustrated in Fig. 1, which is a pressure–composition isotherm of a metal–hydrogen system. As hydrogen is dissolved in a metal, the H_2 pressure in equilibrium with the solid solution increases with hydrogen concentration. When the solubility limit is reached at point y, the nonstoichiometric hydride phase, MH_x , is formed. Because there is now an additional phase in the system, the number of degrees of freedom decreases in accordance with the phase rule, and the H_2 pressure remains constant across the concentration range from y to x. Therefore, the appearance of a plateau pressure is indicative of new phase (hydride) formation. The plateau pressure represents the dissociation P of the hydride at the particular T of the isotherm. As H_2 is added to the system in this concentration range (y to x), hydrogen-saturated metal is converted to nonstoichiometric hydride, MH_x . After the metal is converted to hydride, further addition of H_2 beyond the composition x results in an increase in H_2 pressure as the composition approaches the stoichiometric value, s. Therefore, the stoichiometry range of the hydride, x to s, also can be obtained from such isotherms. Most hydrides discussed in this chapter are nonstoichiometric, and the deviation from the stoichiometric composition (s–x) may be large.

In the initial solution of H_2 in metals, the solubility is proportional to the square root of the H_2 pressure. This suggests that hydrogen is dissolved in the atomic rather than the molecular state. Structural investigations support and confirm this notion. Consequently, the heat of dissociation of H_2 , E_D , which is 436 kJ/mol H_2 , represents an energy barrier to the reaction and influences the rate of the reaction. Reaction (a) can be considered a three-stage process, consisting of H_2 adsorption on the metal surface, solution into the bulk and nucleation of the hydride phase. For the first stage, adsorption of H_2 on a clean metal surface¹, potential-energy curves for a metal and an H_2 molecule and for a metal and two H atoms can be calculated² as a function of distance from the metal surface. The resulting curves, shown schematically in Fig. 2, reveal two adsorption types, physis- and chemisorption. Physisorption, represented by curve 1, re-

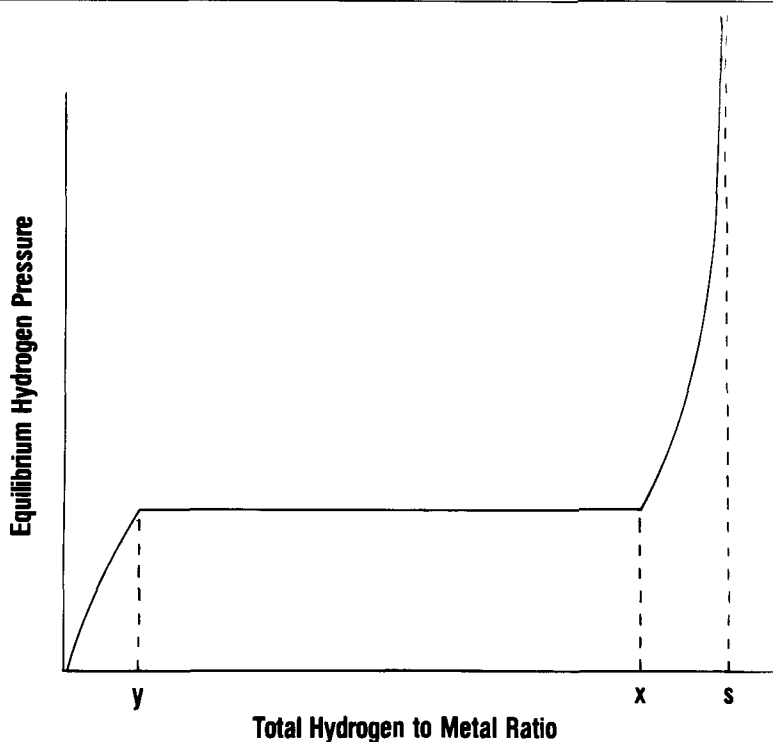


Figure 1. Typical pressure-composition isotherm for a metal-hydrogen system.

sults from attraction by dispersion forces of an H_2 molecule to the metal surface, whereas chemisorption, curve 2, arises from chemical bonding between the H atom and the metal. The minimum in the physisorption curve corresponds to the equilibrium distance of the H_2 molecule from the metal surface and is¹ ca. 0.2–0.3 nm; the heat of adsorption, E_{ad} , is³ < 30 kJ/mol H_2 . By contrast, in the chemisorption curve, the equilibrium distance of the H atom from the metal atom in the surface is¹ 0.05–0.1 nm (i.e., chemical bond length distances), and the heat of chemisorption, E_c , is³ larger, > 100 kJ/mol H_2 .

Hydrogen molecules striking a metal surface can be physisorbed or chemisorbed depending on their kinetic energies and the height of the activation barrier, E_{act} . The activation barrier is determined by the point of intersection of the physisorption curve and the chemisorption curve in relation to the zero-energy level. Intersection above the zero-energy level corresponds to activated chemisorption (as depicted in Fig. 2), whereas intersection below corresponds to nonactivated chemisorption. In the example of Fig. 2, H_2 molecules with kinetic energies $< E_{ad}$ can be adsorbed physically, whereas molecules with energies $> E_{act}$ can move along curve 1 to the intersection with curve 2, change over to curve 2 at the intersection, dissociate into H atoms and become chemisorbed. In the second stage¹ of the process, the chemisorbed H atoms penetrate the surface, a step that may or may not require an activation energy³, and are subse-

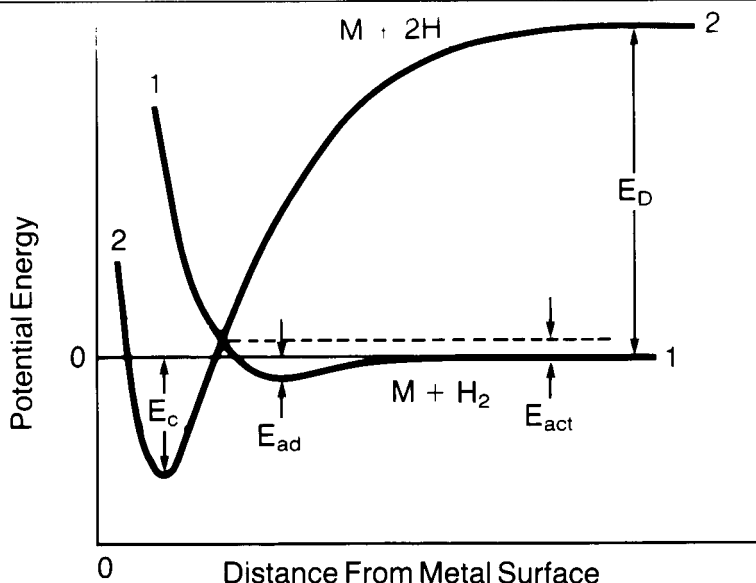


Figure 2. Potential energy as a function of metal–hydrogen distance for hydrogen molecules (curve 1) and for hydrogen atoms (curve 2).

quently dissolved in the bulk through diffusion. The diffusion process also requires an energy of activation, E_{diff} . The final stage is nucleation of the new phase; associated with this stage is an activation energy of nucleation, E_{nucl} . The rate-determining step in this entire process depends on the magnitude of E_{act} , E_c , E_{diff} , E_{nucl} , etc.³

The shapes of the potential-energy curves shown in Fig. 2 are very dependent on the condition of the metal surface; e.g., roughness, cleanliness and crystal orientation³ influence rates. In the practical preparation of metal hydrides according to Eq. (a), surface contamination of the metal is the most serious problem. Most metals after exposure to air do not react with H_2 gas at RT without some form of activation. The activation process consists of the mechanical removal of surface layers (oxides, CO, sulfides, etc.), or by heating to high T in ultrahigh vacuum to evaporate or dissolve the surface-contaminating species. Gaseous H_2 is then admitted to the metal sample without exposure to air. The absorption is carried out at elevated T to increase rate.

The hydrides formed in reaction (a) may be classified as (1) saline or ionic hydrides, (2) metallic hydrides and (3) covalent hydrides. The saline hydrides include the hydrides of the alkali and alkaline-earth metals, except BeH_2 , which is covalent. Transition metals form binary compounds with hydrogen that are classified as metallic hydrides including rare-earth and actinide hydrides. Intermetallic compound hydrides, such as $TiFeH_2$ and $LaNi_5H_6$, may be thought of as pseudobinary metallic hydrides.

The crystal lattices of the saline hydrides consist of hydrogen anions and metal cations, but not exclusively; e.g., in LiH , calculations⁴ and diffraction experiments⁵ suggest that electron transfer from Li to H is 0.8–1 e, implying a strong ionic bond with covalent character. Magnesium hydride occupies a special position. Although classified here as a saline hydride, its properties are intermediate between the ionic hydrides and covalent BeH_2 .

The nature of chemical bonding in metallic hydrides is controversial⁶⁻¹⁰, with two opposing models: the protonic and the ionic. In the former¹¹, hydrogen is assumed to donate its electron to the d band of the transition metal, forming an alloy with the metal. Hydrogen, therefore, exists as protons, partially screened by the conduction electrons in the metal sublattice. The opposing view asserts¹² that H accepts an electron from the metal to form a hydride anion and a metal cation, i.e., a saline hydride type. The protonic model is supported by the metallic conductivity of metallic hydrides. However, the rare-earth trihydrides become semiconductors with electronic properties better explained by the ionic model¹³. The enthalpies of formation of metallic hydrides resemble those of the saline hydrides. However, results from nuclear gamma-ray resonance fluorescence, positron annihilation, magnetic susceptibility and nuclear magnetic resonance (NMR) as well as theoretical considerations are not conclusive, although they are interpreted in terms of one of these two models¹⁰.

Energy-band calculations¹⁴⁻²² can resolve these differences; e.g., in the metallic hydride structure the 1s orbitals of H and the metal-band states mix and hybridize, and in such monohydrides as PdH with H in O_h sites, the sp metal bands mix with the H bonding orbitals to form a modified band, lowered in energy. The energy states of this band are filled below the energy E_F in the metal (where E_F is the electrochemical potential of electrons in the metal), and the added electrons from hydrogen go into the empty metallic states above E_F , and so the hydrogen donates its electron to the metal, i.e., it has the appearance of the proton model. The stability of the hydride is determined by the extent to which the states in the modified band are empty, and by the amount the energy of the modified band is lowered. In dihydrides and trihydrides new low-lying states, associated with the H atoms, are formed, and the additional electrons occupy these states, i.e., as in the ionic model. The energies of the new bands are dependent on the H-H distance, which in turn is determined by the sites occupied by H in the metal sublattice and the size of the metal atom. The positions of the energy bands determine the formation and stability of these hydrides.

(G. G. LIBOWITZ, A. J. MAELAND)

1. R. Speiser, in *Metal Hydrides*, W. M. Muller, J. P. Blackledge, G. G. Libowitz, eds., Academic Press, New York, 1968, p. 51.
2. J. F. Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).
3. L. Schlappbach, A. Seiler, F. Stucki, H. C. Siegmann, *J. Less-Common Met.*, **73**, 145 (1980).
4. H. Shull, *J. Appl. Phys.*, **33**, 292 (1962).
5. R. S. Calder, W. Cochran, D. Griffiths, R. D. Lowde, *J. Phys. Chem. Solids*, **23**, 621 (1962).
6. T. R. P. Gibb, Jr., *Prog. Inorg. Chem.*, **3**, 315 (1962).
7. G. G. Libowitz, *The Solid-State Chemistry of Binary Metal Hydrides*, W. A. Benjamin, New York, 1965; good introduction to the subject.
8. J. P. Blackledge, in *Metal Hydrides*, W. M. Muller, J. P. Blackledge, G. G. Libowitz, eds., Academic Press, New York, 1968, p. 1.
9. K. M. Mackay, *Hydrogen Compounds of the Metallic Elements*, E. & F. N. Spon, London, 1966.
10. G. G. Libowitz, in *MTP Internat. Rev. Sci.*, Vol. 10, *Solid-State Chemistry*, L. E. J. Roberts, ed., Butterworths, London, 1972, p. 79.
11. N. F. Mott, H. Jones, *The Theory of the Properties of Metals and Alloys*, Dover Publications, New York, 1936.
12. G. G. Libowitz, T. R. P. Gibb, Jr., *J. Phys. Chem.*, **60**, 510 (1956).
13. G. G. Libowitz, *Ber. Bunsenges. Phys. Chem.*, **76**, 837 (1972).
14. A. C. Switendick, *Solid-State Commun.*, **8**, 1463 (1970).
15. A. C. Switendick, *Int. J. Quant. Chem.*, **5**, 459 (1971).
16. A. C. Switendick, in *Hydrogen in Metals*, Vol. I, G. Alefeld, J. Völkl, eds., Springer-Verlag, Berlin, 1978, p. 101; review article.

17. A. C. Switendick, *Z. Phys. Chem. N. F., (Frankfurt-am-Main)* 117, 447 (1979); review article.
18. A. C. Switendick, *J. Less-Common Met.*, 101, 191 (1984).
19. D. A. Papaconstantopoulos, in *Metal Hydrides*, G. Bambakidis, ed., Plenum Press, New York, 1981, p. 215; review article.
20. N. I. Kulikov, V. N. Borzunov, A. D. Zvonkov, *Phys. Stat. Sol., B*, 86, 83 (1978).
21. V. I. Savin, R. A. Andriveskii, V. I. Potorocha, V. Ya. Markin, *Inorg. Mater. (Engl. Transl.)*, 14, 1254 (1979).
22. M. Gupta, in *Metal Hydrides*, G. Bambakidis, ed., Plenum Press, New York, 1981, p. 255.

1.12.2. with Alkali Metals.

The reactions of H_2 with the alkali metals are discussed in §1.8.2. The hydrides thus formed are ionic and consist of alkali-metal cations and hydrogen anions, H^- . They resemble the alkali halides, because hydrogen can be considered as the first halogen.

(G. G. LIBOWITZ, A. J. MAELAND)

1.12.3. with Alkaline-Earth Metals.

Direct reaction of Ca, Sr, Ba and presumably Ra with H_2 forms hydrides that are ionic, like the alkali-metal hydrides. Direct reaction with Mg also forms a hydride which may be synthesized by other methods. Alkaline-earth hydrides are discussed in §1.8.3.

(G. G. LIBOWITZ, A. J. MAELAND)

1.12.4. with Group IIIA Transition Metals

The group IIIA transition metals include the lanthanides and actinides, as well as Sc and Y; however, the hydrides of Sc and Y are so similar to those of the lanthanides that they are included with the rare-earth hydrides.

(G. G. LIBOWITZ, A. J. MAELAND)

1.12.4.1. Involving Lanthanides.

The lanthanides form dihydrides and trihydrides with H_2 . The lanthanide hydrides are divided into three groups based on their crystal structures.

The first group consists of hydrides of La, Ce, Pr and Nd. The dihydrides are cubic, with H atoms occupying the T_d sites of a fcc metal sublattice (fluorite structure). The trihydrides of the first group are also cubic and form solid solutions with the dihydrides. The third H per formula unit occupies an O_h site in the fcc metal sublattice. Hydrogen atoms occupy O_h sites before all the T_d sites are filled, so that at the stoichiometric composition, MH_2 , there is an equal concentration of vacant T_d sites and occupied O_h sites¹.

The second subgroup, Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu, also forms fluorite-type dihydrides, but their trihydrides are hexagonal and the dihydride undergoes a phase change on formation of the trihydride. Hexagonal scandium trihydride, $ScH_{2.65}$, can be prepared² only at > 30 MPa H_2 .

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 18. A. C. Switendick, *J. Less-Common Met.*, 101, 191 (1984).
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The third subgroup consists of Eu and Yb dihydrides, which have an orthorhombic structure and resemble the alkaline-earth hydrides, CaH_2 , SrH_2 and BaH_2 (see §1.8.3.3).

The rare-earth hydrides are prepared by heating the metal ($> 200^\circ\text{C}$) under H_2 to initiate the reaction; after equilibrium is reached the sample is slowly cooled to RT. Alternatively, the metal is first heated in vacuum, followed by admission of H_2 gas and slow cooling to RT. Finely divided metal can react with H_2 even at RT. Initial heating removes surface oxidation³ and other surface impurities.

The hydrides are pyrophoric, particularly when finely divided.

Single crystals of Ce hydrides are grown⁴ by forming the compounds from saturated melts (see Fig. 1). A boat containing molten Ce is placed under a thermal gradient such that the lowest T is above the peritectic (ca. 1010°C), and H_2 is slowly dissolved in the melt. When the Ce at the cool end of the boat attains the H content corresponding to the liquidus line between the two-phase (liquid and hydride) region, solid nonstoichiometric Ce hydride, $\text{CeH}_{2-\delta}$, forms (where δ is determined by the composition at the solidus line for the hydride). As further H_2 is added, molten Ce at a higher T solidifies into hydride, so the solid-liquid interface moves toward hotter portions of the melt until completely solidified. In this manner single crystals of Ce hydride may be grown. The rate of growth is controlled by the rate H_2 is introduced into the system.

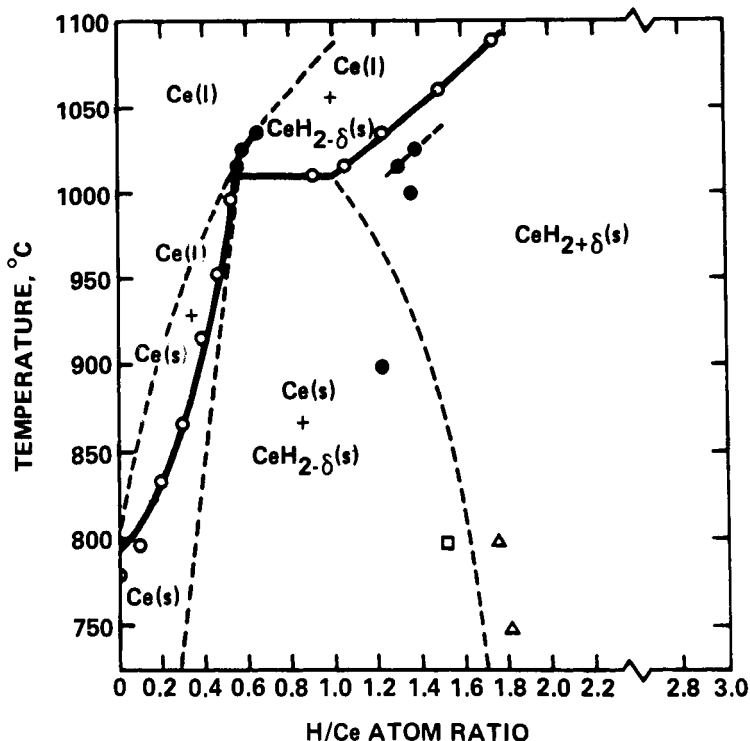
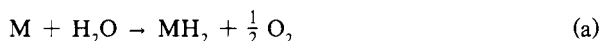


Figure 1. Partial phase diagram for the Ce-H system (From ref. 4).

Neodymium falls into the first group in forming a cubic trihydride. However, if the hydride is prepared at $< 350^{\circ}\text{C}$, a hexagonal Nd trihydride is formed⁵, similar to those in the second group. This trihydride is metastable, however; heating $> 350^{\circ}\text{C}$ transforms it to the cubic phase, and subsequent cooling $< 350^{\circ}\text{C}$ does not reform the hexagonal phase.

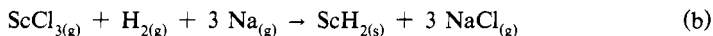
Although Eu forms only a dihydride, a higher hydride of Yb can be prepared⁶ under high H_2 pressure. The Yb is slowly heated to ca. 200°C under 2.2 MPa H_2 and then slowly cooled to RT. The resulting $\text{YbH}_{2.55}$ has a cubic structure similar to that of the first-group trihydrides. Single crystals of Yb dihydride are prepared⁷ by vapor transport, whereby YbH_2 is heated to 900°C for 5–10 h in an evacuated Mo tube. Crystals, 0.01–0.5 mm, deposit in the cooler (550 – 700°C) portions of the tube. Erbium dihydride may also be prepared⁸ by vaporizing Er with high-energy laser pulses under 0.1 MPa of H_2 . The ErH_2 condenses as chains of globular particles, ca. 10.0–12.5 nm.

Rare-earth hydrides are also prepared by methods other than direct reaction with H_2 ; e.g., rare-earth dihydrides can be formed from the metal with H_2O vapor at 100 – 150°C :

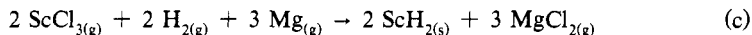


for Nd⁹, Gd^{10,11} and Dy^{9,11}. Equation (a) is thermodynamically unfavorable, but the product may be stabilized by the presence of oxygen incorporated into the solid hydride phase¹¹.

Scandium dihydride may be prepared¹² by chemical-vapor deposition:



or:



Hydrogen alone is not a strong enough reducing agent, so Na or Mg must be used. The ScH_2 is deposited as brittle, black crystals sufficiently downstream from the chloride deposits that the hydride is free of chloride.

(G. G. LIBOWITZ, A. J. MAELAND)

1. G. G. Libowitz, A. J. Maeland, in *Handbook on the Physics and Chemistry of Rare Earths*, K. A. Gschneidner, L. Eyring, eds., North-Holland, Amsterdam, 1979, p. 299.
2. I. O. Bashkin, E. G. Ponyatovskii, M. E. Kost, *Phys. Status Solidi B*, **87**, 369 (1978).
3. L. C. Beavis, R. S. Blewer, J. W. Guthrie, E. J. Nowak, W. G. Perkins, in *Proc. Hydrogen Economy, Miami Energy Conf.*, T. N. Veziroglu, ed., Univ. of Miami, Coral Gables, FL, 1974, p. S4-38.
4. G. G. Libowitz, J. G. Pack, in *Proc. Internat. Conf. Crystal Growth*, H. S. Peiser, ed., Pergamon Press, Oxford, 1967, p. 129; *Inorg. Synth.*, **4**, 184 (1973).
5. M. H. Mintz, Z. Hadari, M. Bixon, *J. Less-Common Met.*, **37**, 331 (1974).
6. J. C. Warf, K. Hardcastle, *J. Am. Chem. Soc.*, **83**, 2206 (1961); *Inorg. Chem.*, **5**, 1728 (1966).
7. J. M. Haschke, M. R. Clark, *High-Temp. Sci.*, **7**, 152 (1975).
8. H. Oesterreicher, H. Bittner, B. Kothari, *J. Solid-State Chem.*, **26**, 97 (1978).
9. J. Dexpert-Ghys, C. Loier, Ch. H. Blanchetais, P. E. Caro, *J. Less-Common Met.*, **41**, 105 (1975).
10. H. Oesterreicher, H. Bittner, K. Shuler, *J. Solid-State Chem.*, **29**, 191 (1979).
11. H. K. Smith, A. G. Moldovan, R. S. Craig, W. E. Wallace, S. G. Sankar, *J. Solid-State Chem.*, **32**, 239 (1980).
12. T. Kobayashi, H. Takei, *J. Cryst. Growth*, **45**, 29 (1978).

1.12.4.2. Involving Actinides.

Actinides react directly with H_2 to form hydrides of different stoichiometries. Thorium forms a tetragonal dihydride, related to the fluorite structure, and a higher hydride, Th_4H_{15} , which has a complex bcc structure. The trihydrides of U and Pa have the bcc β -W structure, and U also forms a low-T trihydride with a different bcc structure. Hydrides similar to the third group of the lanthanides (see §1.12.4.1), i.e., an fcc dihydride and a hexagonal trihydride, are formed by Np through Bk.

The hydrides are prepared like the lanthanide hydrides, i.e., by heating the metal to react with H_2 gas followed by slow cooling. Some finely powdered metals react with hydrogen at RT.

The direct synthesis of AcH_2 is unknown. It is present only in samples of Ac metal prepared by reducing¹ $AcCl_3$ with hydrogen, which may have come from residual hydrogen in the reaction of $Ac(OH)_3$ and NH_4Cl to form the $AcCl_3$.

Structural changes and volume expansion on forming the hydride from the metal produce powdered hydride. However, Th_4H_{15} is prepared in massive form by preparing the hydride² at 850°C and 75 MPa.

The low-T form of UH_3 can be prepared by cathodic charging of U metal in a solution of $HClO_4$ or NaOH below 20°C, in addition to direct reaction with H_2 gas at -40°C.

(G. G. LIBOWITZ, A. J. MAELAND)

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1.12.5. with Group IVA Transition Metals

Nonstoichiometric hydrides that have cubic CaF_2 -type structures or a tetragonally distorted version form when Ti, Zr and Hf react with H_2 ¹. The hydride phases have wide composition ranges that depend on T. The limiting composition is MH_2 .

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Titanium hydride is prepared by heating Ti in H_2 at atmospheric P. The reaction is slow below 300°C but increases¹ with T; optimum is 400–500°C. Because surface impurities impede the reaction, an initial outgassing step to 1000°C in vacuum is helpful in dissolving the surface oxide or other impurities. After equilibration with H_2 at the reaction T, the sample is cooled slowly to RT in H_2 to achieve maximum hydrogen content, TiH_2 .

The hydride is also prepared electrochemically^{2,3} by cathodic charging of Ti in 1 N H_2SO_4 . Hydride formation, however, is limited to a thin surface layer^{2,3} owing to slow hydrogen diffusion.

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2. P. Millenbach, M. Givon, *J. Less-Common Met.*, 87, 179 (1982).
3. E. Brauer, R. Gruner, F. Rauch, *Ber. Bunsenges. Phys. Chem.*, 87, 341 (1983).

1.12.5.2. Involving Zirconium.

The preparation of ZrH_2 follows the procedure as in §1.12.5.1 for TiH_2 . In the Zr-H_2 system the oxide layer reduces¹ the rate markedly below 250°C. Sintering Ni to Zr catalyzes H_2 absorption and compensates for the effect of the oxide layer, improving the rate below 250°C; this may be important for getter applications¹.

Cathodic charging² also is used to prepare ZrH_2 . Hydride formation again is limited to a thin surface layer as in the formation of TiH_2 by the same method.

(G. G. LIBOWITZ, A. J. MAELAND)

1. G. Kuus, W. Martens, *J. Less-Common Met.*, 75, 111 (1980).
2. E. Brauer, R. Gruner, F. Rauch, *Ber. Bunsenges. Phys. Chem.*, 87, 341 (1983).

1.12.5.3. Involving Hafnium.

The procedure for HfH_2 is the same as for TiH_2 (see §1.12.5.1). The optimum T, however, is higher than for TiH_2 or ZrH_2 . To obtain reasonable rates, T should be¹ at least $\geq 500^\circ\text{C}$.

The hydride also has been made in thin surface layers by cathodic charging².

(G. G. LIBOWITZ, A. J. MAELAND)

1. R. K. Edwards, E. Veleckis, *J. Phys. Chem.*, 66, 1657 (1962).
2. B. Streb, E. Brauer, *Z. Metallkd.*, 74, 680 (1983).

1.12.6. with Group VA Transition Metals.

The nonstoichiometric monohydrides formed by V, Nb and Ta have structures that are determined by T and the H content^{1,2}. Order-disorder transitions involving the H atoms lead to structural complexity; in the ordered phases the bcc metal lattice distorts to tetragonal, orthorhombic or monoclinic. In addition, V and Nb, but not Ta, at >0.1 MPa H_2 form dihydrides that have the fluorite structure. Hence, the phase diagrams of these elements with H_2 are complex.

The group VA metals do not react with H_2 at RT because an oxide layer on the surface of the metal³⁻⁷ prevents or inhibits the catalytic dissociation of H_2 and the subsequent solution in the metal. Even in the absence of an oxide layer, however, there is an intrinsic barrier to H_2 absorption because of a strongly bound surface state of hydrogen^{8,9}. Activation procedures consequently are required before the reaction with H_2 proceeds at an appreciable rate, e.g., heating to 300–500°C and utilizing absorption-desorption cycles or heating to high T in ultrahigh vacuum to dissolve⁷ the surface film before H_2 is admitted in situ.

The rate of H_2 absorption by the group VA metals is increased by thin overlayers⁸⁻¹² of Pd or Pt; Ni and Fe are less effective, and Cu and Ag have no appreciable effect, at least not with¹³ Ta. The solution of small amounts of a second metal yields alloys that react rapidly with H_2 at RT without activation¹⁴. The second metal should have a radius $\geq 5\%$ smaller than that of the solvent group VA metal, e.g., Co, Fe and Ni.

1. E. A. Gulbransen, K. F. Andrew, *Trans. A.I.M.E.*, **185**, 741 (1949).
2. P. Millenbach, M. Givon, *J. Less-Common Met.*, **87**, 179 (1982).
3. E. Brauer, R. Gruner, F. Rauch, *Ber. Bunsenges. Phys. Chem.*, **87**, 341 (1983).

1.12.5.2. Involving Zirconium.

The preparation of ZrH_2 follows the procedure as in §1.12.5.1 for TiH_2 . In the Zr-H_2 system the oxide layer reduces¹ the rate markedly below 250°C. Sintering Ni to Zr catalyzes H_2 absorption and compensates for the effect of the oxide layer, improving the rate below 250°C; this may be important for getter applications¹.

Cathodic charging² also is used to prepare ZrH_2 . Hydride formation again is limited to a thin surface layer as in the formation of TiH_2 by the same method.

(G. G. LIBOWITZ, A. J. MAELAND)

1. G. Kuus, W. Martens, *J. Less-Common Met.*, **75**, 111 (1980).
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1.12.5.3. Involving Hafnium.

The procedure for HfH_2 is the same as for TiH_2 (see §1.12.5.1). The optimum T, however, is higher than for TiH_2 or ZrH_2 . To obtain reasonable rates, T should be¹ at least $\geq 500^\circ\text{C}$.

The hydride also has been made in thin surface layers by cathodic charging².

(G. G. LIBOWITZ, A. J. MAELAND)

1. R. K. Edwards, E. Veleckis, *J. Phys. Chem.*, **66**, 1657 (1962).
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The reaction of Nb with H_2 occurs readily with $LaNi_5$, which acts as a catalyst¹⁵; e.g., Nb powder mixed with activated $LaNi_5$ (50 : 1) absorbs H_2 to give¹⁵ NbH_2 at $\geq 22^\circ C$.

Treating the metals or the monohydrides with 10% HF yields^{16,17} NbH_2 and VH_2 . Atomic hydrogen is generated from the metal with HF and subsequently is absorbed by the metal or the monohydride. Atomic H generated by other sources, such as the thermal dissociation of H_2 on heated W filaments¹⁸, also may be used, but the hydrogen concentration is difficult to regulate.

Electrochemical charging also yields hydrides of the group VA metals¹⁹, e.g., NbH_2 is formed¹⁹ when Nb metal is made the cathode in an electrolyte solution such as H_3PO_4 or H_2SO_4 ; however, chemical dissolution of the metal occurs and the hydrogen concentration in the sample is difficult to control.

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1. H. Asano, M. Hirabayashi, *Z. Phys. Chem. N.F. (Frankfurt-am-Main)*, **114**, 1 (1979).
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9. M. A. Pick, *Phys. Rev. B*, **24**, 4287 (1981).
10. N. Boes, H. Züchner, *Z. Naturforsch. Teil A*, **31**, 754 (1976).
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12. T. Schober, A. Carl, *J. Less-Common Met.*, **63**, P53 (1979).
13. K. Nakamura, H. Uchida, E. Fromm, *J. Less-Common Met.*, **80**, P19 (1981).
14. A. J. Maeland, G. G. Libowitz, J. F. Lynch, G. Rak, *J. Less-Common Met.*, **104**, 133 (1984).
15. D. H. W. Carstens, J. D. Farr, *J. Inorg. Nucl. Chem.*, **36**, 461 (1974).
16. G. Brauer, H. Müller, *Angew. Chem.*, **70**, 53 (1958).
17. A. J. Maeland, T. R. P. Gibb Jr., D. P. Schumacher, *J. Am. Chem. Soc.*, **83**, 3728 (1961).
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1.12.7. with Groups VIA, VIIA and VIII Transition Metals

Except for Pd, the groups VIA, VIIA and VIII metals do not form hydrides under ordinary conditions of T and H_2 pressure. If, however, the thermodynamic activity of hydrogen is increased by going to high P, these metals do react. The required pressures are > 10 MPa and special high-P equipment is therefore necessary for the synthesis of these hydrides.

(G.G. LIBOWITZ, A.J. MAELAND)

1.12.7.1. Involving Chromium and Molybdenum.

Hydrides of the bcc group VIA elements Cr and Mo, but not W, are prepared by high-P techniques¹⁻⁶. Chromium hydride is synthesized¹ directly from Cr with H_2 by keeping a thin Cr foil at $150^\circ C$ under 2200 MPa for 4 h. The H/Cr atom ratio is 0.93 and the metal lattice structure hcp^{1,3,5,6}. The hydride, therefore, is equivalent

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to the hexagonal hydride phase prepared earlier⁸ by electrodeposition of Cr from H_2SO_4 . A dihydride phase (fcc) also results from this procedure, but this phase is not prepared by the direct reaction. The formation pressure (plateau pressure observed in absorption) is^{3,4} 1.74–1.82 GPa at 150°C, whereas the decomposition pressure, i.e., plateau pressure observed in desorption, at the same T is 0.32 GPa. This hysteresis is observed frequently in metal–hydrogen systems.

Nearly stoichiometric MoH is prepared² at 350°C and high H_2 pressure; the formation pressure^{2,6} at this T is 23.5 GPa. X-Ray diffraction analysis², performed at –145°C because of the instability of the hydride, shows an hcp Mo lattice. The volume expansion on formation of the hydride phase ($\Delta V_{\text{Mo}} = V_{\text{MoH}} - V_{\text{Mo}}$) is approximately the same as in the Cr system, 20% vs. 19%, respectively². An fcc dideuteride, MoD_2 , forms in thin films during bombardment of Mo with D_2^+ ions⁷. This phase is the counterpart of the fcc CrH_2 phase prepared electrochemically⁸.

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2. I. T. Belash, V. E. Antonov, E. G. Ponyatovskii, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **235**, 665 (1977).
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7. V. Kh. Alimov, A. E. Gorodetskii, A. P. Zakharov, V. M. Sharapov, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **241**, 595 (1978).
8. C. A. Snavely, *Trans. Electrochem. Soc.*, **92**, 552 (1947).

1.12.7.2. Involving Manganese and Technetium.

Treating Mn with H_2 at 2.2 GPa and RT gives no evidence of hydride formation¹. However, at 300°C and 1.4 GPa, MnH forms¹. The need for the higher T arises from kinetic barriers (surface contamination), which must be overcome before hydrogen absorption takes place^{1,2}. Hydride formation is confirmed at^{3,4} 1.8 GPa H_2 and 350°C. These pressures are higher than the absorption plateau pressures²; e.g., at 448°C, the plateau pressure is only 0.56 GPa and at 729°C it is 1.04 GPa. The maximum hydrogen content, H/Mn, is ca. 0.8, and hydride formation changes the metal-lattice structure from cubic to hexagonal^{1–5}. Despite the lower absorption pressures observed in the formation of MnH as compared to CrH and the similarity in their structures, Mn does not form a hydride phase during cathodic codeposition or cathodic saturation with H_2 , whereas Cr does².

The preparation of TcH occurs⁶ at 300°C and 1.9 GPa H_2 with the composition $\text{TcH}_{0.73}$. Both $\text{TcH}_{0.73}$ and the hydrogen-free metal have an hcp metal lattice, which makes it difficult, without extensive x-ray work showing the dependence of lattice parameters on composition, to determine whether $\text{TcH}_{0.73}$ is a hydride phase or just a solid solution of hydrogen in Tc. However, from the behavior of the electrical resistance of TcH as a function of composition, it can be deduced that a hydride phase is formed⁶ below 300°C.

There are no reports of hydride formation in the Re– H_2 system.

(G.G. LIBOWITZ, A.J. MAELAND)

1.12. Formation of Reversible Metal Hydrides

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1.12.7. with Groups VIA, VIIA and VIII Transition Metals

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4. E. G. Ponyatovskii, V. E. Antonov, I. T. Belash, *Inorg. Mater. (Engl. Transl.)*, **14**, 1227 (1978); review.
5. B. Baranowski, *Z. Phys. Chem. N. F. (Frankfurt-am-Main)*, **114**, 59 (1979); review.
6. V. I. Spitsyn, E. G. Ponyatovskii, V. E. Antonov, I. T. Belash, O. A. Balakhovskii, *Proc. Acad. Sci. USSR (Engl. Trans.)*, **247**, 723 (1979).

1.12.7.3. Involving Nickel, Rhodium and Palladium.

Nearly stoichiometric NiH is prepared¹ at RT by exposing Ni foil to > 1.0 GPa H_2 . The formation pressure^{2,3} at RT is actually ca. 0.6 GPa. The decomposition pressure of the hydride at RT is, in contrast, 0.34 GPa, indicating considerable hysteresis in this system²⁻⁷. During hydride formation the Ni lattice remains fcc but undergoes⁸ a sudden 18% increase in volume⁸.

Nickel hydride also can be prepared⁹ by cathodic charging of Ni in aq H_2SO_4 in the presence of a promoter (e.g., As); this delays the recombination of H atoms into molecules at the Ni surface, enhancing the concentration of active hydrogen².

Rhodium hydride is prepared¹⁰ at 250°C and > 4.0 GPa H_2 (the formation pressure)^{6,8}. Maximum concentration of hydrogen in the hydride is $H/Rh = 0.65$ at 6.0 GPa. The hydride has an fcc metal lattice like Rh itself, but with a lattice parameter¹⁰ ca. 6% larger than that of pure Rh.

Palladium hydride can be prepared without high H_2 pressures; e.g., at 30°C the equilibrium absorption pressure¹¹ is ca. 2.40 kPa; at 160°C, 203 kPa and even at 250°C it is only 1.11×10^3 kPa. The reaction is slow at RT, however, unless activated (Pd black) material is used¹¹. Heating to 100–200°C speeds up the reaction when H_2 pressures greater than the dissociation pressure of hydride are maintained¹¹. The hydride is formed by cathodic charging in aqueous electrolytes as well as by immersing Pd in aq H_2SO_4 and bubbling H_2 gas through¹¹⁻¹³. The composition of the hydride at atmospheric pressure of H_2 and RT is^{11,12} ca. $PdH_{0.7}$. The metal lattice in the hydride has the same structure as in the metal phase, i.e., fcc, but expanded by 10.8%. Near stoichiometric PdH can be prepared at RT by increasing the H_2 pressure³ to 1.2 GPa or by electrolytic charging^{11,12}.

Hydrogen is soluble in Co at high pressures^{8,14}; at 6.5 GPa and 225°C the equilibrium composition is $CoH_{0.51}$. However, the solubility varies smoothly with pressure, indicating a continuous solid solution rather than hydride formation^{8,14}.

(G.G. LIBOWITZ, A.J. MAELAND)

1. B. Baranowski, R. Wisniewski, *Bull. Acad. Polon. Sci.*, **14**, 273 (1966); *Chem. Abstr.*, **65**, 14,810 (1966).
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4. B. Baranowski, in *Metal Hydrides*, G. Bambakidis, ed., Plenum Press, New York, 1981, p. 193; review.
5. T. Skoskiewicz, *Phys. Status Solidi*, **A**, **6**, 29 (1971).
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7. B. Baranowski, K. Bochenska, *Rocz. Chem.*, **38**, 1419 (1964); *Chem. Abstr.*, **62**, 9825 (1965).

1. M. Krukowski, B. Baranowski, *Rocz. Chem.*, **49**, 1183 (1975); *Chem. Abstr.*, **83**, 150,966 (1975).
2. B. Baranowski, in *Hydrogen in Metals*, Vol II, G. Alefeld, J. Völk, eds., Springer-Verlag, Berlin, 1978, p. 157; review.
3. E. G. Ponyatovskii, I. T. Belash, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **224**, 570 (1975).
4. E. G. Ponyatovskii, V. E. Antonov, I. T. Belash, *Inorg. Mater. (Engl. Transl.)*, **14**, 1227 (1978); review.
5. B. Baranowski, *Z. Phys. Chem. N. F. (Frankfurt-am-Main)*, **114**, 59 (1979); review.
6. V. I. Spitsyn, E. G. Ponyatovskii, V. E. Antonov, I. T. Belash, O. A. Balakhovskii, *Proc. Acad. Sci. USSR (Engl. Trans.)*, **247**, 723 (1979).

1.12.7.3. Involving Nickel, Rhodium and Palladium.

Nearly stoichiometric NiH is prepared¹ at RT by exposing Ni foil to > 1.0 GPa H₂. The formation pressure^{2,3} at RT is actually ca. 0.6 GPa. The decomposition pressure of the hydride at RT is, in contrast, 0.34 GPa, indicating considerable hysteresis in this system²⁻⁷. During hydride formation the Ni lattice remains fcc but undergoes⁸ a sudden 18% increase in volume⁸.

Nickel hydride also can be prepared⁹ by cathodic charging of Ni in aq H₂SO₄ in the presence of a promoter (e.g., As); this delays the recombination of H atoms into molecules at the Ni surface, enhancing the concentration of active hydrogen².

Rhodium hydride is prepared¹⁰ at 250°C and > 4.0 GPa H₂ (the formation pressure)^{6,8}. Maximum concentration of hydrogen in the hydride is H/Rh = 0.65 at 6.0 GPa. The hydride has an fcc metal lattice like Rh itself, but with a lattice parameter¹⁰ ca. 6% larger than that of pure Rh.

Palladium hydride can be prepared without high H₂ pressures; e.g., at 30°C the equilibrium absorption pressure¹¹ is ca. 2.40 kPa; at 160°C, 203 kPa and even at 250°C it is only 1.11×10^3 kPa. The reaction is slow at RT, however, unless activated (Pd black) material is used¹¹. Heating to 100–200°C speeds up the reaction when H₂ pressures greater than the dissociation pressure of hydride are maintained¹¹. The hydride is formed by cathodic charging in aqueous electrolytes as well as by immersing Pd in aq H₂SO₄ and bubbling H₂ gas through¹¹⁻¹³. The composition of the hydride at atmospheric pressure of H₂ and RT is^{11,12} ca. PdH_{0.7}. The metal lattice in the hydride has the same structure as in the metal phase, i.e., fcc, but expanded by 10.8%. Near stoichiometric PdH can be prepared at RT by increasing the H₂ pressure³ to 1.2 GPa or by electrolytic charging^{11,12}.

Hydrogen is soluble in Co at high pressures^{8,14}; at 6.5 GPa and 225°C the equilibrium composition is CoH_{0.51}. However, the solubility varies smoothly with pressure, indicating a continuous solid solution rather than hydride formation^{8,14}.

(G.G. LIBOWITZ, A.J. MAELAND)

1. B. Baranowski, R. Wisniewski, *Bull. Acad. Polon. Sci.*, **14**, 273 (1966); *Chem. Abstr.*, **65**, 14,810 (1966).
2. B. Baranowski, *Ber. Bunsenger. Phys. Chem.*, **76**, 714 (1972); review.
3. B. Baranowski, in *Hydrogen in Metals*, Vol. II, G. Alefeld, E. Völk, eds., Springer-Verlag, Berlin, 1978, p. 157; review.
4. B. Baranowski, in *Metal Hydrides*, G. Bambakidis, ed., Plenum Press, New York, 1981, p. 193; review.
5. T. Skoskiewicz, *Phys. Status Solidi*, **A**, **6**, 29 (1971).
6. B. Baranowski, *Z. Phys. Chem. N.F. (Frankfurt-am-Main)*, **114**, 59 (1979); review.
7. B. Baranowski, K. Bochenska, *Rocz. Chem.*, **38**, 1419 (1964); *Chem. Abstr.*, **62**, 9825 (1965).

8. E. G. Ponyatovskii, V. E. Antonov, I. T. Belash, *Inorg. Mater. (Engl. Trans.)*, **14**, 1227 (1978); review.
9. B. Baranowski, M. Smialowski, *J. Phys. Chem. Solids*, **12**, 206 (1959).
10. V. E. Antonov, I. T. Belash, V. F. Degtyareva, E. G. Ponyatovskii, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **239**, 222 (1978).
11. F. A. Lewis, *The Palladium-Hydrogen System*, Academic Press, London, 1967.
12. B. Siegel, G. G. Libowitz, in *Metal Hydrides*, W. M. Mueller, J. P. Blackledge, G. G. Libowitz, eds., Academic Press, New York, 1968, p. 545.
13. T. B. Flanagan, F. A. Lewis, *J. Phys. Chem.*, **29**, 1417 (1958).
14. I. T. Belash, V. E. Antonov, E. G. Ponyatovskii, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **235**, 128 (1977).

1.12.8. to Form Ternary Hydrides

1.12.8.1. from Intermetallics

The formation of hydrides of intermetallic compounds by direct reaction with H_2 is carried out at lower T than formation of binary hydrides, and more rapidly. However, disproportionation of the intermetallic compound may occur at elevated T .

The known hydrides of intermetallics can be classified in a few groups, and the discussion in this section is in terms of those groups.

Most binary intermetallic compounds that form hydrides contain one hydride-forming element (e.g., group IVA, VA, VIA, rare earth or actinide) and one which does not form hydrides under normal conditions (but may under ultra-high P , e.g., group VIII); see §1.12.7. Because bonds to the hydride-forming elements are stronger, hydrogen atoms are found in lattice sites in which the hydride-forming elements are nearest neighbors.

(G. G. LIBOWITZ, A. J. MAELAND)

1.12.8.1.1. Giving AM_5 Compounds.

The AM_5 intermetallic compounds have the hexagonal $CaCu_5$ structure. For the compounds that form hydrides, A is usually a rare-earth element (or Ca or Th) and M is either Ni or Co (but may also be Fe , Pt or Cu). These hydrides are listed in Table 1 along with the minimum H_2 pressure needed to form the hydride and the approximate hydrogen content of the hydride, x .

Because of hysteresis effects¹⁶ the pressure for formation of the hydride may be higher than the dissociation pressure shown in Fig. 1, §1.12.1. The values of x shown in Table 1 are the approximate hydrogen content of the hydride when it is formed initially, but they usually increase with H_2 pressure. At high pressure (150 MPa), the maximum possible hydrogen content in these intermetallic compounds is nine H atoms per formula unit¹⁷.

The pressure necessary to form the hydride may be changed by partial substitution of one of the components by other metals; e.g., the replacement of 20% of the La in $LaNi_5$ with Nd doubles the formation pressure³; the pressure may also be raised³ by replacing some of the Ni and Pd . Conversely, substitutions, such as Al for Ni , decrease the hydride formation pressure¹⁸.

The intermetallic compound is usually prepared by arc melting the elements in the correct proportions under Ar . To insure homogeneity, the alloy is remelted several times. Samples also are prepared by induction melting.

8. E. G. Ponyatovskii, V. E. Antonov, I. T. Belash, *Inorg. Mater. (Engl. Trans.)*, **14**, 1227 (1978); review.
9. B. Baranowski, M. Smialowski, *J. Phys. Chem. Solids*, **12**, 206 (1959).
10. V. E. Antonov, I. T. Belash, V. F. Degtyareva, E. G. Ponyatovskii, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **239**, 222 (1978).
11. F. A. Lewis, *The Palladium-Hydrogen System*, Academic Press, London, 1967.
12. B. Siegel, G. G. Libowitz, in *Metal Hydrides*, W. M. Mueller, J. P. Blackledge, G. G. Libowitz, eds., Academic Press, New York, 1968, p. 545.
13. T. B. Flanagan, F. A. Lewis, *J. Phys. Chem.*, **29**, 1417 (1958).
14. I. T. Belash, V. E. Antonov, E. G. Ponyatovskii, *Proc. Acad. Sci. USSR (Engl. Transl.)*, **235**, 128 (1977).

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The pressure necessary to form the hydride may be changed by partial substitution of one of the components by other metals; e.g., the replacement of 20% of the La in $LaNi_5$ with Nd doubles the formation pressure³; the pressure may also be raised³ by replacing some of the Ni and Pd. Conversely, substitutions, such as Al for Ni, decrease the hydride formation pressure¹⁸.

The intermetallic compound is usually prepared by arc melting the elements in the correct proportions under Ar. To insure homogeneity, the alloy is remelted several times. Samples also are prepared by induction melting.

TABLE 1. HYDRIDES OF AM₅ INTERMETALLICS

Intermetallic	x ^a	P (MPa) ^b	Ref.
YNi ₅	1	30	1
	3.5	100	
YCo ₅	2.8	3	2
LaNi ₅	6.7	0.13	3
LaCo ₅	3.2	0.004	4
	4.4	0.02	
LaCu ₅	2.5	0.024	5
LaPt ₅	ca. 1.5	20	1
	ca. 2.5	62	
	4	105	
CeNi ₅	6	4.8	7
CeCo ₅	2.7	0.16	8
CeFe ₅	ca. 4	0.075	9
PrNi ₅	ca. 6	0.8	6
PrCo ₅	ca. 3		
		ca. 0.07	10
NdNi ₅	6	1.3	6
NdCo ₅	3.5	0.08	11
SmNi ₅	ca. 4	3	6
SmCo ₅	2.6	0.5	12
EuNi ₅	> 2		13
GdNi ₅	3	1.2	6
GdCo ₅	2.5	ca. 0.3	11
YbNi ₅	2.9	ca. 1.2	6
ThCo ₅	4.6	ca. 5	14, 2
CaNi ₅	1	0.0025	15
	4.5	0.056	
	6.5	2.7	

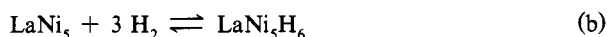
^a x = number of H atoms per formula unit.^b P = maximum H₂ pressure needed to form hydride.

These intermetallic compounds react with H₂ at RT, provided that the pressure is high enough¹⁹, but there is often an induction period ranging from seconds to days depending on previous treatment of the alloy and time of exposure to air²⁰. Freshly prepared samples not exposed to air usually react in seconds because of the catalytic action^{21,22} of Ni and Co on Fe. The intermetallic compound is oxidized at its surface to form the rare-earth oxide (e.g., La₂O₃) and free metallic Ni (or Co or Fe), which acts as a catalyst to dissociate H₂. Impurity gases, such as CO, O₂ and H₂O, decrease the rates of hydride formation and can poison the alloy for reaction²³⁻²⁵ with H₂.

The formation of most hydrides of intermetallic compounds is metastable with respect to disproportionation of the intermetallic compound; e.g., the free energy of:



is more negative than that for:



However, the hydride of the intermetallic compound forms because it is kinetically fa-

vored. Reaction (a) requires rearrangement of metal atoms, which is unlikely to occur at low T, whereas reaction (b) involves little motion of metal atoms. However, at elevated T, reaction (a) is more likely to occur; e.g., LaNi_5H_6 degrades²⁶ at 300°C, and CaNi_5H_x disproportionates¹⁵ at even lower T.

The H atoms in the AM_5 compounds occupy two types of T_d sites in the lattice; in one hydrogen is coordinated to two A atoms and two M atoms, and in the second to one A and three M atoms²⁷. However, the bonds must occur between the A and the H atoms because the M atoms do not form hydrides.

(G. G. LIBOWITZ, A. J. MAELAND)

1. T. Takeshita, K. A. Gschneidner, J. F. Lakner, *J. Less-Common Met.*, **78**, 43 (1981).
2. T. Takeshita, W. E. Wallace, R. S. Craig, *Inorg. Chem.*, **13**, 2282 (1974).
3. H. H. Van Mal, K. H. J. Buschow, A. R. Miedema, *J. Less-Common Met.*, **35**, 65 (1974).
4. F. A. Kuipers, B. O. Loopstra, *J. Phys. Chem. Solids*, **35**, 301 (1974).
5. J. Shinar, D. Shaltiel, D. Davidov, A. Grayevsky, *J. Less-Common Met.*, **60**, 209 (1978).
6. J. L. Anderson, T. C. Wallace, A. L. Bowman, C. L. Radosevich, M. L. Courtney, USAEC Report No. LA-5320-MS (Los Alamos Scientific Laboratory), July, 1973; *Chem. Abstr.*, **80**, 125,151 (1974).
7. C. E. Lundin, F. E. Lynch, AFOSR Report No. F44620-74-C-002 (Denver Research Institute), 1976.
8. F. A. Kuipers, *J. Less-Common Met.*, **27**, 27 (1972).
9. C. E. Lundin, F. E. Lynch, AFOSR Report No. TR-75-1482 (Denver Research Institute), 1975.
10. J. Clinton, H. Bittner, H. Oesterreicher, *J. Less-Common Met.*, **41**, 187 (1975).
11. F. A. Kuipers, *Ber. Bunsenges. Phys. Chem.*, **76**, 1220 (1972).
12. J. S. Raichlen, R. H. Doremus, *J. Appl. Phys.*, **42**, 3166 (1971).
13. F. W. Oliver, K. W. West, R. L. Cohen, K. H. J. Buschow, *J. Phys., F: Met. Phys.*, **8**, 701 (1978).
14. K. H. J. Buschow, H. H. Van Mal, A. R. Miedema, *J. Less-Common Met.*, **42**, 163 (1975).
15. G. D. Sandroock, J. J. Murray, M. L. Post, J. B. Taylor, *Mater. Res. Bull.*, **17**, 887 (1982).
16. G. G. Libowitz, *The Solid State Chemistry of Binary Metal Hydrides*, W. A. Benjamin, New York, 1965, p. 83.
17. J. F. Lakner, F. S. Uribe, S. A. Steward, *J. Less-Common Met.*, **72**, 87 (1980).
18. M. H. Mendelsohn, D. M. Gruen, A. E. Dwight, *Nature (London)*, **269**, 45 (1977).
19. J. H. N. van Vucht, F. A. Kuipers, H. C. A. M. Bruning, *Philips Res. Rep.*, **25**, 133 (1970); *Chem. Abstr.*, **73**, 28,184 (1970).
20. H. H. Van Mal, Ph.D. Thesis, Technical Univ., Delft, Neth., 1976.
21. H. C. Siegmann, L. Schlapbach, C. R. Brundle, *Phys. Rev. Lett.*, **40**, 972 (1978).
22. W. E. Wallace, R. F. Karlicek, H. Imamura, *J. Phys. Chem.*, **83**, 1708 (1979).
23. G. D. Sandroock, P. D. Goodell, *J. Less-Common Met.*, **73**, 161 (1980).
24. P. D. Goodell, *J. Less-Common Met.*, **89**, 45 (1983).
25. F. G. Eisenberg, P. D. Goodell, *J. Less-Common Met.*, **89**, 55 (1983).
26. R. L. Cohen, K. W. West, J. H. Wernick, *J. Less-Common Met.*, **73**, 273 (1980).
27. P. Fischer, A. Furrer, G. Busch, L. Schlapbach, *Helv. Phys. Acta*, **50**, 421 (1977).

1.12.8.1.2. Giving AB_2 Compounds.

The AB_2 intermetallics discussed here have either a cubic MgCu_2 -type or a hexagonal MgZn_2 -type structure where A has a metallic radius larger than that of B, ideally by a factor of 1.225. The radius ratios of A to B vary from ca. 1.05 to 1.68, but the radii contract or expand on compound formation to approach the ideal value¹ of 1.225.

The unit cell of the cubic structure has 136 T_d interstices, or 17 per formula unit. Many of these interstices are available for occupancy by hydrogen. However, the hydrogen content in these hydrides is generally under seven atoms per formula unit, as seen in Table 1. The maximum number of H atoms per formula unit is given by the

1.12. Formation of Reversible Metal Hydrides 251
 1.12.8. to Form Ternary Hydrides
 1.12.8.1. from Intermetallics

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5. J. Shinar, D. Shaltiel, D. Davidov, A. Grayevsky, *J. Less-Common Met.*, **60**, 209 (1978).
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20. H. H. Van Mal, Ph.D. Thesis, Technical Univ., Delft, Neth., 1976.
21. H. C. Siegmann, L. Schlapbach, C. R. Brundle, *Phys. Rev. Lett.*, **40**, 972 (1978).
22. W. E. Wallace, R. F. Karlicek, H. Imamura, *J. Phys. Chem.*, **83**, 1708 (1979).
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The unit cell of the cubic structure has 136 T_d interstices, or 17 per formula unit. Many of these interstices are available for occupancy by hydrogen. However, the hydrogen content in these hydrides is generally under seven atoms per formula unit, as seen in Table 1. The maximum number of H atoms per formula unit is given by the

TABLE 1. HYDRIDES OF AB_2 INTERMETALLICS

Compound	x^a	P (kPa) ^b	Ref.
CaAl ₂	2 (0.1)	ND	2
ScMn ₂	3.8 (3)	ca. 10^{-3}	3, 4
ScFe ₂	3.1 (3)	6×10^{-1}	3, 4
ScCo ₂	2.2 (0.1)	ND	5
ScNi ₂	2.0 (0.1)	ND	5
TiBe ₂	ca. 3 (> 15)	ND	6
TiCr ₂	2 (7)	ND	7
TiMn _{1.5}	2.6 (5)	7×10^2	8
YMg ₂	3.2 (3)	ND	3
YMn ₂	3.4 (0.1–5)	ND	9
YFe ₂	4.3 (1.1)	6×10^1	10
YCo ₂	4.2 (0.1–5)	5	9, 11
YNi ₂	3.6 (0.1–5)	ND	9
ZrV ₂	5.3 (1.2)	ca. 10^{-2}	4, 11
ZrCr ₂	4 (6.1)	ca. 2×10^{-1}	11
ZrMn ₂	3.6 (0.8)	10^{-1}	11
ZrTa ₂	2.4 (NR)	ND	12
LaMg ₂	6.4 (3)	ND	2
LaNi ₂	4.6 (3–5)	ND	13
LaRu ₂	4.5 (0.34)	6×10^{-4}	4, 11
LaRh ₂	4.9 (6)	5×10^2 ($x \approx 1$) 1 ($x \approx 2$)	11, 14
CeMg ₂	6.2 (3)	ND	3
CeFe ₂	4 (NR)	ND	15
CeCo ₂	4.1 (1)	ND	16
CeNi ₂	4 (4)	ND	17
CeRu ₂	5.2 (1)	ND	11
PrCo ₂	4.0 (6)	ND	18
PrNi ₂	4.4 (6)	ND	18
NdMg ₂	4 (2.8)	ND	2
NdFe ₂	3.0 (6)	ND	18
NdNi ₂	3.7 (6)	ND	18
NdRu ₂	5.5 (NR)	4×10^{-3}	4
SmMg ₂	3 (0.2)	ND	2
SmMn ₂	4.2 (3)	ND	3
SmFe ₂	2.9 (6)	ND	18
SmCo ₂	3.2 (3)	ND	3
SmNi ₂	3.8 (6)	ND	18
SmRu ₂	4.6 (5)	3×10^{-2}	4, 19
EuNi ₂	> 2 (17)	ND	20
EuRh ₂	3 (NR)	ND	21
GdMn ₂	3 (1.5–2)	6×10^{-7}	14
GdFe ₂	4.7 (1.1)	20 2.3×10^2 ($x \approx 2$)	10
GdCo ₂	4.5 (6.1)	2×10^1 ($x \approx 3$) 6×10^1 ($x \approx 3.5$)	11, 14
GdNi ₂	4.35 (6)	3.5×10^{-7}	14
GdRu ₂	4.5 (0.34)	ND	11, 22
GdRh ₂	4.9 (6)	ND	11

TABLE 1. HYDRIDES OF AB₂ INTERMETALLICS (CONTINUED)

Compound	x ^a	P (kPa) ^b	Ref.
TbCo ₂	3.2 (6)	ND	18
TbNi ₂	3.5 (6)	ND	18
DyMn ₂	3.4 (15)	ND	23
DyFe ₂	7.7 (14)	5 × 10 ⁻⁴ (x = 1.5) 2 × 10 ⁻³ (x = 2.0) 3 (x = 3.4) 100 (x = 4.3) 10 ³ (x = 5)	24, 25
DyCo ₂	3.8 (6)	ND	18
DyNi ₂	3.6 (6)	ND	18
DyRu ₂	3.1 (1)	ND	26
HoFe ₂	4.5 (3.6)	ND	27
HoCo ₂	3.8 (6)	ND	18
HoNi ₂	3.8 (6)	ND	18
HoRu ₂	4.2 (NR)	2.6 × 10 ⁻¹	4, 28
ErMn ₂	4.6 (6.5)	1.5	29
ErFe ₂	4.1 (13)	5 × 10 ⁻³ (x = 1.4) 5 × 10 ⁻¹ (x ≈ 2.3) 2 (x ≈ 3.2) 700 (x ≈ 4.0)	25, 30
ErCo ₂	3.65 (3.6)	ND	31
ErNi ₂	3.6 (6)	ND	18
ErRu ₂	NR	8.5 × 10 ¹	4
TmFe ₂	4.6 (3.6)	6.8 × 10 ⁻³ (x = 1.6) 5.3 (x = 3.4) > 1.3 × 10 ³ (x = 4.2)	27, 32
YbNi ₂	3.1 (1)	ND	26
LuFe ₂	4 (NR)	ND	33
HfV ₂	4.5 (3.4)	5 × 10 ⁻⁵	4, 34
ThRu ₂	5 (5.9)	ND	11

^a NR, not reported.

^b ND, not determined.

value of x in column 2. The numbers in parenthesis represent the H₂ pressure (in MPa) at which the x values are determined.

The third column gives the dissociation pressures of the hydride phase at RT. These are the minimum pressures required to form the hydride. For some cases (e.g., GdCo₂) there is more than one hydride phase. These hydrides are usually more stable than the hydrides of the AM₂ compounds (see §1.12.8.1.1); i.e., the dissociation pressures are much lower but, as with the AM₂ compounds, the stability and maximum hydrogen content can be modified by changing the stoichiometry or by alloying with other elements. For example, TiMn₂ only absorbs ca. 0.1 H atoms per formula unit at the stoichiometric composition; however, as the composition becomes Mn deficient, the hydrogen content increases to 2.6 H atoms per formula unit⁸.

The effect of additional alloying elements can be illustrated with ZrMn₂, the hydride of which has a dissociation pressure of 0.1 kPa (see Table 1). The addition of 0.8

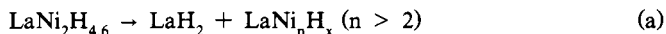
mol Fe increases³⁵ the dissociation pressure to 30 kPa, whereas 0.8 mol Co raises it to 400 kPa.

The intermetallics themselves are synthesized by melting together the elements in the correct proportions either by arc melting under an inert atmosphere (usually Ar gas) or by induction melting. The alloys are remelted several times to make them more homogeneous. To insure homogeneity the samples are then annealed at 600–950°C for 24 h to 2 weeks.

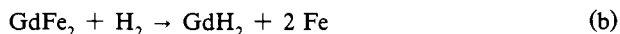
Although some intermetallics react directly with H_2 with no activation, some activation procedure is required for most; e.g., for the rare-earth Ni, Co and Fe compounds⁴ the alloy is evacuated and heated at 70°C for 1.5 h and at 250°C for 1.5 h. After it has cooled to RT the sample alloy is contacted with 5–10 MPa of H_2 and becomes fully hydrided in 15 min to 3 h. Pulverizing the sample may be necessary before it can react with H_2 ; e.g., $TiMn_{1.5}$ is pulverized to 5–20 mesh (0.8 to 4 mm), evacuated at RT for 1.2 h and then contacted⁸ with H_2 at 4.5 MPa. Likewise, $CeCo_2$ that is crushed to –20 to +60 mesh (0.25 to 0.8 mm) in a glove box forms the hydride after evacuation and contact with H_2 at 1 MPa and RT.

The mechanism of hydride formation of $ZrMn_2$ and $TiMn_{1.5}$ is related to segregation and preferential oxidation of the Mn on the surface³⁶ and precipitation of metallic Zr and Ti at the subsurface below the oxidized Mn. The Zr and Ti metallic precipitates catalyze the $H_2 \rightleftharpoons 2 H$ reaction. In addition, the Zr and Ti precipitates themselves may form hydrides and spill over atomic H to the intermetallic compound lying below.

Because the AB_2 hydrides have a greater tendency to disproportionate than the AB_3 compounds, T must be kept sufficiently low during preparation of the hydride to prevent disproportionation. For example, $LaNi_2H_{4.5}$ is prepared by hydriding³⁷ $LaNi_2$ at 25°C and 10 MPa of H_2 ; however, at 100°C decomposition to LaH_3 occurs. Heating $LaNi_2H_{4.6}$ to 400°C gives³⁸:



The heat of hydride formation can cause local excursions in T that disproportionate the hydride: in attempts to prepare the hydride of $GdFe_2$ by exposing to H_2 at 1.3 MPa, the resulting hydride contains only 3.4 H atoms per formula unit, and the hydrogen could not be desorbed¹⁰. Therefore, local heating resulting from rapid hydrogen absorption gives:



More gentle hydrogenation at 0.2 MPa and 20°C (after activation) and then increasing the pressure to 1.3 MPa forms the hydride $GdFe_2H_{4.73}$.

The AB_2 intermetallics (vide supra) have three types of interstices that may be available for occupation by H atoms². In all three, the H atoms would be T_d coordinated. There are 12 sites per formula unit in which the coordination is to two A and two B atoms, four sites with coordination to one A and three B atoms, and one with coordination to four B atoms. Because the A atoms are normally the hydride-forming elements, the H atoms should prefer the (2 A + 2 B) sites, for this would give maximum bonding to the A atoms; in the ZrB_2 compounds (B = Cr, Mn, V) the (2 Zr + 2 B) sites are the first to be occupied^{39–41} and at higher concentrations of hydrogen the (1 Zr + 3 B) sites also become occupied. In ZrV_2 the number of atoms in the (1 Zr + 3 V) sites exceeds that in the (2 Zr + 2 V) sites^{40,42}. However, V is also a hydride former⁴³, although it

does not form as strong a bond with hydrogen as does Zr. There is no evidence for occupation of the 4 B sites by hydrogen.

1. J. H. Wernick, in *Intermetallic Compounds*, J. H. Westbrook, ed., Wiley, New York, 1967, p. 197.
2. D. Shaltiel, *J. Less-Common Met.*, **62**, 407 (1978).
3. M. E. Kost, M. V. Raevskaya, A. L. Shilov, E. I. Yaropolova, V. I. Mikheeva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **24**, 1803 (1979).
4. A. L. Shilov, L. N. Padurets, M. E. Kost, *Russ. J. Phys. Chem. (Engl. Transl.)*, **57**, 555 (1983).
5. V. V. Burnasheva, A. V. Ivanov, V. A. Yartys, K. N. Semenenko, *Inorg. Mater. (Engl. Transl.)*, **17**, 704 (1981).
6. A. J. Maeland, G. G. Libowitz, *J. Less-Common Met.*, **89**, 197 (1983).
7. I. Jacob, A. Stern, A. Moran, D. Shaltiel, D. Davidov, *J. Less-Common Met.*, **73**, 369 (1980).
8. T. Gamo, Y. Moriwaki, N. Yanagihara, T. Yamashita, T. Iwaki, in *Hydrogen Energy Progress*, T. N. Veziroglu, ed., Pergamon Press, Oxford, 1981, p. 2127.
9. H. H. VanMal, K. H. J. Buschow, A. R. Miedema, *J. Less-Common Met.*, **49**, 473 (1976).
10. H. A. Kierstead, *J. Less-Common Met.*, **86**, L1 (1982).
11. D. Shaltiel, I. Jacob, D. Davidov, *J. Less-Common Met.*, **53**, 117 (1977).
12. H. W. Newkirk, USERDA Report UCRL-52110 (Lawrence Livermore Laboratory), Aug., 1976; *Chem. Abstr.*, **87**, 120,446 (1977).
13. V. I. Mikheeva, M. E. Kost, A. L. Shilov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **23**, 657 (1978).
14. I. Jacob, D. Shaltiel, *J. Less-Common Met.*, **65**, 117 (1979).
15. K. H. J. Bushow, *Solid State Commun.*, **19**, 421 (1976).
16. R. A. Guidotti, G. B. Atkinson, M. M. Wong, *J. Less-Common Met.*, **52**, 13 (1977).
17. R. H. Van Essen, K. H. J. Buschow, *J. Less-Common Met.*, **70**, 189 (1980).
18. V. V. Burnasheva, A. V. Ivanov, K. N. Semenenko, *Inorg. Mater. (Engl. Transl.)*, **14**, 1017 (1978).
19. A. L. Shilov, E. I. Yaropolova, M. V. Raevskaya, M. E. Kost, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **23**, 1871 (1978).
20. F. W. Oliver, K. W. West, R. L. Cohen, K. H. J. Buschow, *J. Phys. F: Met. Phys.*, **8**, 701 (1978).
21. R. L. Cohen, K. W. West, K. H. J. Buschow, *Solid State Commun.*, **25**, 293 (1978).
22. S. K. Malik, W. E. Wallace, *Solid State Commun.*, **24**, 283 (1977).
23. R. L. Cohen, K. W. West, F. Oliver, K. H. J. Buschow, *Phys. Rev., B*, **21**, 941 (1980).
24. F. Pourarian, W. E. Wallace, A. Elatter, J. F. Lakner, *J. Less-Common Met.*, **74**, 161 (1980).
25. H. A. Kierstead, *J. Less-Common Met.*, **70**, 199 (1980).
26. H. Oesterreicher, K. Ensslen, E. Bucher, *Appl. Phys.*, **22**, 303 (1980).
27. D. M. Gualtieri, K. S. V. L. Narasimhan, W. E. Wallace, *A.I.P. Conf. Proc.*, **34**, 219 (1976); *Chem. Abstr.*, **86**, 49,910 (1977).
28. A. L. Shilov, M. E. Kost, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **26**, 163 (1981).
29. P. J. Viccaro, G. K. Shenoy, D. Niarchos, B. D. Dunlap, *J. Less-Common Met.*, **73**, 265 (1980).
30. T. B. Flanagan, N. B. Mason, G. E. Biehl, *J. Less-Common Met.*, **91**, 107 (1983).
31. D. M. Gualtieri, W. E. Wallace, *J. Less-Common Met.*, **55**, 53 (1977).
32. H. A. Kierstead, *J. Less-Common Met.*, **85**, 213 (1982).
33. K. H. J. Buschow, P. H. Smit, R. M. van Essen, *J. Magn. Magnet. Mater.*, **15-18**, 1261 (1980).
34. P. Duffer, D. M. Gualtieri, V. U. S. Rao, *Phys. Rev. Lett.*, **37**, 1410 (1976).
35. F. Pourarian, V. K. Sinha, W. E. Wallace, *J. Less-Common Met.*, **96**, 237 (1984).
36. L. Schlapbach, *J. Less-Common Met.*, **89**, 37 (1983).
37. H. Oesterreicher, J. Clinton, H. Bittner, *Mater. Res. Bull.*, **11**, 1241 (1976).
38. M. E. Kost, A. L. Shilov, *Inorg. Mater. (Engl. Transl.)*, **14**, 1270 (1978).
39. J. J. Didisheim, K. Yvon, D. Shaltiel, P. Fischer, *Solid State Commun.*, **31**, 47 (1979).
40. J. J. Didisheim, K. Yvon, P. Fischer, D. Shaltiel, *J. Less-Common Met.*, **73**, 355 (1980).

41. D. Fruchart, A. Rouault, C. B. Shoemaker, D. P. Shoemaker, *J. Less-Common Met.*, **73**, 363 (1980).
42. J. J. Didisheim, K. Yvon, D. Shaltiel, P. Fischer, P. Bujard, E. Walker, *Solid State Commun.*, **32** 1087 (1979).
43. G. G. Libowitz, *Solid State Chemistry of Binary Metal Hydrides*, W. A. Benjamin, New York, 1965, pp. 66, 76.

1.12.8.1.3. Giving Hydrides of Other Intermetallics.

Although the AM_5 $CaCu_5$ -type and AB_2 ($MgCu_2$ and $MgZn_2$ types) compound hydrides are most extensively covered, other hydrides of intermetallics are known (see Table 1). The formation of these hydrides is similar to those of the AM_5 and AB_2 hydrides.

The AM_3 intermetallics ($CeNi_3$ type) can be considered derivatives of the AM_5 and AB_2 compounds⁷. The AM_3 structure is obtained by stacking one unit of AM_5 onto one unit of AB_2 (see §1.12.8.1.2). Consequently, the sites available for occupation by H atoms are the same as those in the AM_5 and AB_2 intermetallics. Similarly, the A_2M_7 (Cu_2Ni_7 -type) structure may be formed by two layers of AM_5 and one layer of AB_2 . The equilibrium dissociation pressures (i.e., minimum H_2 pressure necessary to form the hydride at RT) are ca. 0.01–50 kPa for the AM_3 and 0.1–1000 kPa for the A_2M_7 hydrides.

The A_6M_{23} intermetallics have a complex fcc structure with 116 atoms (four formula units) per unit cell⁸. Although there are many interstices available for occupation by hydrogen, the preferred sites are those that are coordinated by one or more atoms of the metal that forms a stable hydride (i.e., the A atom)⁹. Dissociation pressures range^{10,11} 0.4–300 kPa.

Hydrides are made from 1 : 1 intermetallics of groups V and VIII transition metals. For example, TiFe, TiCo and TiNi have the cubic CsCl structure, but on hydriding the first two form monohydrides and dihydrides that are orthorhombic and monoclinic, respectively, although they may be viewed as distorted CsCl structures. No hydride phase is formed from TiNi at RT (or above), but a solid solution of maximum composition $TiNiH_{1.47}$ forms¹². The ZrCo and HfCo intermetallics also have the CsCl structure but transform to the orthorhombic CrB structure on formation of a monohydride

TABLE 1. HYDRIDES OF INTERMETALLIC COMPOUNDS

Intermetallic general formula	Examples of hydrides	Ref.
AM_3 (A = rare earth, Y, Th; M = Fe, Co, Ni)	$CeNi_3H_3$, $YFe_3H_{4.8}$ $LuCo_3H_{3.5}$	1 1 2
A_2M_7 (A = rare earth, Y, Th; M = Fe, Co, Ni)	$Ce_2Co_7H_6$, $Y_2Ni_7H_2$ $Th_2Fe_7H_{6.1}$	1 1 3
A_6M_{23} (A = rare earth, Y, Th; M = Fe, Ni)	$Y_6Fe_{23}H_{22.5}$ $Th_6Mn_{23}H_{30}$	1 4
AB (A = Ti, Zr, Hf; B = Fe, Co, Ni)	TiFeH, TiFeH ₂ ZrNiH, ZrNiH ₃	5 6

1.12. Formation of Reversible Metal Hydrides

1.12.8. to Form Ternary Hydrides

1.12.8.1. from Intermetallics

41. D. Fruchart, A. Rouault, C. B. Shoemaker, D. P. Shoemaker, *J. Less-Common Met.*, **73**, 363 (1980).
42. J. J. Didisheim, K. Yvon, D. Shaltiel, P. Fischer, P. Bujard, E. Walker, *Solid State Commun.*, **32**, 1087 (1979).
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A_6M_{23} (A = rare earth, Y, Th; M = Fe, Ni)	$Y_6Fe_{23}H_{22.5}$ $Th_6Mn_{23}H_{30}$	1 4
AB (A = Ti, Zr, Hf; B = Fe, Co, Ni)	$TiFeH$, $TiFeH_2$ $ZrNiH$, $ZrNiH_3$	5 6

or trihydride, whereas ZrNi and HfNi already have the CrB structure before they form monohydrides and dihydrides of the same structure. Dissociation pressures for hydrides in this group range from 2×10^{-6} kPa for ZrCo monohydride¹³ to 1000 kPa for TiFe dihydride⁵.

Most of these alloys require activation to react with H₂; e.g., HfCo and HfNi are heated at 50°C for a few hours at 4 MPa of H₂ to effect complete absorption¹⁴ of H₂ and TiCo is activated by heating at 325°C for 20 min at 2 MPa of H₂. The alloy is then cooled to RT and more H₂ added. Hydrogen is then desorbed from the sample and then reabsorbed according to the above procedure. After a few such absorption-desorption cycles the sample can be hydrided fully¹⁵. It may be necessary to activate¹⁶ ZrNi by heating in vacuum at 800°C, introducing H₂ into the system after cooling and then reheating under H₂ to 400–450°C. However, it is not necessary to activate this alloy if it is kept under Ar after buffing and cleaning with emory paper⁶. Also ZrCo requires no activation as it reacts¹³ with H₂ at 200°C under a pressure of only 3 kPa.

Because of its low cost and appropriate dissociation pressures, the hydrides of TiFe (along with LaNi₃) are considered for H₂ storage, but TiFe that has been exposed to air does not react with H₂ unless it is activated by granulating to 10 mesh (2 mm), heating to 400°C (in H₂ or vacuum) followed by cooling to RT and applying H₂ at ca. 6 MPa. If the sample is in ingot form, several hydriding and dehydriding cycles are required. The alloy is dehydrided by heating to 200°C while outgassing. Activation^{17,18} also occurs on substituting a few % Mn, Cr, Co, Ni or Nb for Fe. The mechanism of activation of TiFe is still unknown¹⁹. Two mechanisms are possible. One involves the formation of oxides on the surface, primarily Fe₂Ti₄O, that either catalyze the dissociation of H₂ or absorb and transmit hydrogen to the underlying TiFe. The other²⁰ involves segregation of Ti at the surface, oxidation to TiO₂, and reduction of the Fe (by H₂) to metallic Fe. Dissociation of the H₂ occurs on the Fe particles that are formed. Evidence²¹ for the first mechanism is the appearance of Ti₄Fe₂O on the surface of a TiFe sample which undergoes heat treatment simulating the activation procedure under 0.1-Pa dynamic pressure of O₂. Evidence for the second mechanism is the observation^{19,22} of TiO₂ and Fe clusters on the surface on reaction of TiFe with O₂. Discrepancies in the effects of activation on the TiFe samples may result from differences in the preparation conditions¹⁹.

The interstices occupied by hydrogen in the hydrides of the AB compounds are those in which the coordination is predominantly to hydride-forming elements. In ZrNiH₃²³ and ZrCoH₃²⁴ the H atoms are in two sites, T_d sites coordinated by three Zr and one Ni atom, and five-coordinated sites of four Zr and one Ni. In the monohydride of TiFe, the coordination is²⁵ distorted O_h to four Ti and two Ni. However, in all three cases, the H atoms are 9–25% closer to the non-hydride-forming element (Ni or Co) than to the hydride-forming element (Zr or Ti). In the dihydride of FeTi there are four types of distorted O_h sites²⁶; in three the coordination is similar to that in the monohydride. However, in the fourth site, the H atoms are coordinated to four Ni and two Ti. The last type of site is difficult to fill (because of weak H—Fe bonding) and explains why stoichiometric TiFeH₂ cannot be attained. In the monohydride of ZrNi, the H atoms are T_d coordinated to four Zr atoms²⁷.

Other hydrides of intermetallic compounds include the A₂M₇ (A = rare earth, M = Ni, Co)²⁸ or the MoSi₂ structure intermetallics (where Mo = Cu, Pd; Si = Ti, Zr, Hf)²⁹, etc.³⁰. The formation of these hydrides does not differ from that of those already covered; however, because of their technological value, the formation of Mg₂Ni hydrides is discussed.

Pulverizing the alloy to -25 mesh (< 0.7 mm) (in a dry box), loading into a high-pressure reactor and exposing to H_2 at ca. 2.4 MPa at $350^\circ C$ yields³¹ Mg_2NiH_4 . The alloy reacts slowly at ca. 2 MPa and $325^\circ C$. The kinetics improve after several hydriding-dehydriding cycles so that reaction occurs at $200^\circ C$ and 1.4 MPa. The intermetallic compound is hexagonal, but there are two forms of the hydride: a high-T antiferroite cubic form³² ($> 240^\circ C$) and a low-T form which is probably monoclinic³³ ($< 236^\circ C$). As in the AB hydrides, the H atom coordination is predominantly to the hydride-forming elements, four Mg and one Ni atom³². However, the Ni-H distance, 0.147 nm, is closer than the Mg-H distance, 0.230 nm.

The dissociation pressure of Mg_2NiH_4 at RT is³¹ ca. 800 Pa.

(G. G. LIBOWITZ, A. J. MAELAND)

1. R. H. Van Essen, K. H. J. Buschow, *J. Less-Common Met.*, **70**, 189 (1980).
2. H. A. Kierstead, *J. Less-Common Met.*, **96**, 133 (1984).
3. K. H. J. Buschow, H. H. VanMal, A. R. Miedema, *J. Less-Common Met.*, **42**, 163 (1975).
4. S. K. Malik, T. Takeshita, W. E. Wallace, *Solid State Commun.*, **23**, 599 (1977).
5. J. J. Reilly, R. H. Wiswall, *Inorg. Chem.*, **13**, 218 (1974).
6. G. G. Libowitz, H. F. Hayes, T. R. P. Gibb, *J. Phys. Chem.*, **62**, 76 (1958).
7. B. D. Dunlap, P. J. Viccaro, G. K. Shenoy, *J. Less-Common Met.*, **74**, 75, 1980.
8. J. V. Florio, R. E. Rundle, A. I. Snow, *Acta. Crystallogr.* **5**, 449 (1952).
9. D. G. Westlake, *Scripta Metall.*, **16**, 1049 (1982).
10. H. K. Smith, W. E. Wallace, R. S. Craig, *J. Less-Common Met.*, **94**, 89 (1983).
11. S. K. Malik, G. T. Bayer, E. B. Boltich, W. E. Wallace, *J. Less-Common Met.*, **98**, 109 (1984).
12. R. Burch, N. B. Mason, *Z. Phys. Chem. N.F. (Frankfurt-am-Main)*, **116**, 185 (1979).
13. S. J. C. Irvine, I. R. Harris, *J. Less-Common Met.*, **74**, 33 (1980).
14. R. M. Van Essen, K. H. J. Buschow, *J. Less-Common Met.*, **64**, 277 (1979).
15. R. Burch, N. B. Mason, *J. Chem. Soc., Faraday Trans.*, **1**, 75, 561 (1979).
16. L. N. Padurets, A. A. Chertkov, V. I. Mikheeva, *Inorg. Mater. (Engl. Transl.)*, **14**, 1267 (1978).
17. M. H. Mintz, S. Voknin, S. Biderman, Z. Hadari, *J. Appl. Phys.*, **52**, 463 (1981).
18. T. Sasai, K. Oku, H. Konno, K. Onouwe, S. Kashu, *J. Less-Common Met.*, **89**, 281 (1983).
19. H. Züchner, G. Kirch, *J. Less-Common Met.*, **99**, 143 (1984).
20. L. Schlapbach, T. Riesterer, *Appl. Phys.*, **A32**, 169 (1983).
21. A. Venkert, M. Talianker, M. P. Dariel, *Mater. Lett.*, **2**, 45 (1983).
22. H. Züchner, U. Bilitewski, G. Kirch, *J. Less-Common Met.*, **101**, 441 (1984).
23. S. W. Peterson, V. N. Sadana, W. L. Korst, *J. Phys. (Paris)*, **25**, 451 (1964).
24. A. V. Irodova, V. A. Somenkov, S. Sh. Shil'shtein, L. N. Padurets, A. A. Chertkov, *Sov. Phys.-Crystallogr.*, **23**, 591 (1978).
25. P. Thompson, M. A. Pick, F. Reidinger, L. M. Corliss, J. M. Hastings, J. J. Reilly, *J. Phys. F: Met. Phys.*, **8**, L75 (1978).
26. P. Thompson, J. J. Reilly, F. Reidinger, J. M. Hastings, L. M. Corliss, *J. Phys. F: Met. Phys.*, **9**, L62 (1979).
27. D. G. Westlake, H. Shaked, P. R. Mason, B. R. McCart, M. H. Mueller, *J. Less-Common Met.*, **88**, 17 (1982).
28. K. H. J. Buschow, in *Handbook on the Physics and Chemistry of Rare Earths* Vol. 6, K. A. Gschneidner, L. Eyring, eds., North-Holland, Amsterdam, 1984, p. 1.
29. A. J. Maeland, G. G. Libowitz, *J. Less-Common Met.*, **74**, 295 (1980).
30. K. H. J. Buschow, P. C. P. Bouton, A. R. Miedema, *Rep. Prog. Phys.*, **45**, 937 (1982).
31. J. J. Reilly, R. H. Wiswall, *Inorg. Chem.*, **7**, 2254 (1968).
32. J. Schefer, P. Fischer, W. Hälgl, F. Stucki, L. Schlapbach, J. J. Didisheim, K. Yvon, A. F. Andresen, *J. Less-Common Met.*, **74**, 65 (1980).
33. A. F. Andresen, *J. Less-Common Met.*, **88**, 1 (1982).

1.12.8.2. from Metal-Nonmetal Systems

Hydrogen reacts with metal borides, carbides, silicides, nitrides, phosphides, oxides, sulfides, and halides to form a solid solution of hydrogen in the compound with

Pulverizing the alloy to -25 mesh (<0.7 mm) (in a dry box), loading into a high-pressure reactor and exposing to H_2 at ca. 2.4 MPa at $350^\circ C$ yields³¹ Mg_2NiH_4 . The alloy reacts slowly at ca. 2 MPa and $325^\circ C$. The kinetics improve after several hydriding-dehydriding cycles so that reaction occurs at $200^\circ C$ and 1.4 MPa. The intermetallic compound is hexagonal, but there are two forms of the hydride: a high-T antiferroite cubic form³² ($>240^\circ C$) and a low-T form which is probably monoclinic³³ ($<236^\circ C$). As in the AB hydrides, the H atom coordination is predominantly to the hydride-forming elements, four Mg and one Ni atom³². However, the Ni-H distance, 0.147 nm, is closer than the Mg-H distance, 0.230 nm.

The dissociation pressure of Mg_2NiH_4 at RT is³¹ ca. 800 Pa.

(G. G. LIBOWITZ, A. J. MAELAND)

1. R. H. Van Essen, K. H. J. Buschow, *J. Less-Common Met.*, **70**, 189 (1980).
2. H. A. Kierstead, *J. Less-Common Met.*, **96**, 133 (1984).
3. K. H. J. Buschow, H. H. VanMal, A. R. Miedema, *J. Less-Common Met.*, **42**, 163 (1975).
4. S. K. Malik, T. Takeshita, W. E. Wallace, *Solid State Commun.*, **23**, 599 (1977).
5. J. J. Reilly, R. H. Wiswall, *Inorg. Chem.*, **13**, 218 (1974).
6. G. G. Libowitz, H. F. Hayes, T. R. P. Gibb, *J. Phys. Chem.*, **62**, 76 (1958).
7. B. D. Dunlap, P. J. Viccaro, G. K. Shenoy, *J. Less-Common Met.*, **74**, 75, 1980.
8. J. V. Florio, R. E. Rundle, A. I. Snow, *Acta. Crystallogr.* **5**, 449 (1952).
9. D. G. Westlake, *Scripta Metall.*, **16**, 1049 (1982).
10. H. K. Smith, W. E. Wallace, R. S. Craig, *J. Less-Common Met.*, **94**, 89 (1983).
11. S. K. Malik, G. T. Bayer, E. B. Boltich, W. E. Wallace, *J. Less-Common Met.*, **98**, 109 (1984).
12. R. Burch, N. B. Mason, *Z. Phys. Chem. N.F. (Frankfurt-am-Main)*, **116**, 185 (1979).
13. S. J. C. Irvine, I. R. Harris, *J. Less-Common Met.*, **74**, 33 (1980).
14. R. M. Van Essen, K. H. J. Buschow, *J. Less-Common Met.*, **64**, 277 (1979).
15. R. Burch, N. B. Mason, *J. Chem. Soc., Faraday Trans.*, **1**, 75, 561 (1979).
16. L. N. Padurets, A. A. Chertkov, V. I. Mikheeva, *Inorg. Mater. (Engl. Transl.)*, **14**, 1267 (1978).
17. M. H. Mintz, S. Voknin, S. Biderman, Z. Hadari, *J. Appl. Phys.*, **52**, 463 (1981).
18. T. Sasai, K. Oku, H. Konno, K. Onouwe, S. Kashu, *J. Less-Common Met.*, **89**, 281 (1983).
19. H. Züchner, G. Kirch, *J. Less-Common Met.*, **99**, 143 (1984).
20. L. Schlapbach, T. Riesterer, *Appl. Phys.*, **A32**, 169 (1983).
21. A. Venkert, M. Talianker, M. P. Dariel, *Mater. Lett.*, **2**, 45 (1983).
22. H. Züchner, U. Bilutewski, G. Kirch, *J. Less-Common Met.*, **101**, 441 (1984).
23. S. W. Peterson, V. N. Sadana, W. L. Korst, *J. Phys. (Paris)*, **25**, 451 (1964).
24. A. V. Irodova, V. A. Somenkov, S. Sh. Shil'shtein, L. N. Padurets, A. A. Chertkov, *Sov. Phys.-Crystallogr.*, **23**, 591 (1978).
25. P. Thompson, M. A. Pick, F. Reidinger, L. M. Corliss, J. M. Hastings, J. J. Reilly, *J. Phys. F: Met. Phys.*, **8**, L75 (1978).
26. P. Thompson, J. J. Reilly, F. Reidinger, J. M. Hastings, L. M. Corliss, *J. Phys. F: Met. Phys.*, **9**, L62 (1979).
27. D. G. Westlake, H. Shaked, P. R. Mason, B. R. McCart, M. H. Mueller, *J. Less-Common Met.*, **88**, 17 (1982).
28. K. H. J. Buschow, in *Handbook on the Physics and Chemistry of Rare Earths* Vol. 6, K. A. Gschneidner, L. Eyring, eds., North-Holland, Amsterdam, 1984, p. 1.
29. A. J. Maeland, G. G. Libowitz, *J. Less-Common Met.*, **74**, 295 (1980).
30. K. H. J. Buschow, P. C. P. Bouton, A. R. Miedema, *Rep. Prog. Phys.*, **45**, 937 (1982).
31. J. J. Reilly, R. H. Wiswall, *Inorg. Chem.*, **7**, 2254 (1968).
32. J. Schefer, P. Fischer, W. Hälgl, F. Stucki, L. Schlapbach, J. J. Didisheim, K. Yvon, A. F. Andresen, *J. Less-Common Met.*, **74**, 65 (1980).
33. A. F. Andresen, *J. Less-Common Met.*, **88**, 1 (1982).

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distortion of the original lattice or with ordering of the H atoms in the lattice. New structures may be formed. Characteristic of all interactions of H with MX_n compounds (where M is the metal and X the nonmetal) are¹:

1. Only metallic compounds take up hydrogen.
2. The metal must form a hydride.
3. The H atoms preferentially occupy those sites most distant from the X atoms in the lattice. Therefore, only M—H bonds, and no X—H bonds, are formed.

(G. G. LIBOWITZ, J. A. MAELAND)

1.12.8.2.1. Involving Carbides.

Hydrogen forms solid solutions with most carbides. In the hexagonal M_2C structures the H atoms occupy the T_d sites, and in the fcc MC lattices they occupy O_h sites not occupied by C atoms. The solid solutions of hydrogen in these carbides are prepared by heating in H_2 ; e.g., in the carbides V_2C and Nb_2C , solns containing ≤ 0.1 mol fraction of hydrogen are prepared² by introducing H_2 to the carbide at high T, cooling, reheating to high T and evacuating, and then repeating the procedure several times.

With Th carbides, two carbohydride phases, Th_2CH_2 and Th_3CH_4 , are obtained³ by heating the carbide in H_2 gas at 0.1 MPa and 850°C. Pressure–composition isotherms show that these are definite phases, not solid solutions. The Th_2CH_2 is hexagonal and the Th_3CH_4 monoclinic (probably distorted hexagonal). These are stable compounds; extrapolation of the pressure–composition–temperature data to RT indicates dissociation pressures of ca. 10^{-21} and 10^{-14} Pa, respectively. However, the hexagonal Th_2CH_2 transforms⁴ to a cubic phase at 380°C.

Carbohydrides of Yb are prepared⁵ by reacting YbH_2 with graphite for 2–10 h at 900°C under 50 kPa of H_2 . Two carbohydride phases are obtained, a hexagonal $\text{YbC}_{0.5}\text{H}$ and a cubic $\text{YbCH}_{0.5}$.

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3. D. T. Peterson, J. Rexer, *J. Inorg. Nucl. Chem.*, **24**, 519 (1962).
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1.12.8.2.2. Involving Oxides and Sulfides.

Hydrogen forms solid solutions with several metallic oxides, although the solubility is usually less than in the pure metal. This includes ZrO ¹, $\text{Ti}_4\text{M}_2\text{O}$ (where M = Ni, Fe, Co, Cu)^{2–5}, and Zr_2PdO ⁶.

The compound $\text{Zr}_3\text{V}_3\text{O}$ absorbs hydrogen up to the composition $\text{Zr}_3\text{V}_3\text{OH}_{5.5}$ by heating⁷ granules (< 1 mm) of the alloy to 300°C in 0.1–0.2 MPa of H_2 for 0.5–2 h.

The hydrogen molybdenum and tungsten bronzes H_xMoO_3 and H_xWO_3 , where $x = 0.6$, may be prepared by electrochemical reduction of WO_3 or MoO_3 . They violate the condition that the metal must be a hydride former, but they cannot be prepared by direct reaction of the oxide with H_2 , and they differ from other compounds because the hydrogen prefers to bond with oxygen rather than the metal.

The sulfides form solid solutions with no change in structure; Ta_6SH_2 and $\text{Nb}_{21}\text{S}_3\text{H}_5$ are prepared⁹ by outgassing the sulfides at 850–900°C for 4 h, introducing H_2 , cooling to 400°C and holding this T overnight. The sulfides are then reheated to higher T and

1.12. Formation of Reversible Metal Hydrides

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1.12.8. to Form Ternary Hydrides

1.12.8.2. from Metal–Nonmetal Systems

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5. E. Tuscher, H. Bittner, *Monatsh. Chem.*, **111**, 1229 (1980).
6. A. J. Maeland, *J. Less-Common Met.*, **89**, 173 (1983).
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8. R. H. Jarman, P. G. Dickens, *J. Electrochem. Soc.*, **129**, 2276 (1982).
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1.12.8.2.3. Involving Nitrides and Phosphides.

Hydrogen forms solid solutions with phosphides with no structural change. Whereas Pd_3P reacts readily with H_2 at RT or below¹, $\text{Pd}_3\text{P}_{1-x}$ only dissolves hydrogen when it is nonstoichiometric²; i.e., solubility increases with increasing value of x .

Hydrogen also forms solid solutions with nitrides. However, in some Ti nitrohydrides ($\text{TiN}_{1-x}\text{H}_{0.15}$, where $0.16 \leq x \leq 0.26$), ordering of both the N and H atoms occurs at lower T, the N atoms over O_h and the H atoms over the T_d interstices³. Ordering of N in the lattice results from the presence of H atoms. The nitrohydrides are prepared by high-T synthesis of $\text{TiH}_{0.15}$ with N_2 .

In the fcc compound⁴ $\text{ThN}_{1-x}\text{H}_y$, for $x = 0.31$ the maximum value of y is 2.5. The compound is stable; dissociation pressure is ca. 0.1 Pa.

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Many metal-rich transition-metal halides absorb hydrogen reversibly¹⁻³. The halohydrides are prepared by exposing the halide to H_2 at 6–240 kPa and RT–300°C. Faster formation rates are obtained at higher P, but several hours are required to reach maximum hydrogen content. Hemihydrides and monohydrides, $\text{ZrXH}_{0.5}$ and ZrXH , form¹ from ZrCl and ZrBr . Dissociation pressures at RT are ca. 10^{-10} Pa for $\text{ZrClH}_{0.5}$ and $\text{ZrBrH}_{0.5}$ and 10^{-9} Pa for ZrClH and ZrBrH . The H atoms occupy sites in which they are T_d coordinated to four metal atoms⁴. High H_2 pressure may cause disproportionation, e.g.:



Two hydride phases, $\text{ThI}_2\text{H}_{0.7}$ and $\text{ThI}_2\text{H}_{1.7}$, with dissociation pressures at RT of ca. 10^{-4} Pa form² from ThI_2 . Other halohydrides prepared include $\text{LaI}_2\text{H}_{0.75}$, $\text{CeI}_2\text{H}_{0.82}$,

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(G. G. LIBOWITZ, A. J. MAELAND)

1. A. W. Struss, J. D. Corbett, *Inorg. Chem.*, **16**, 360 (1977).
2. A. W. Struss, J. D. Corbett, *Inorg. Chem.*, **20**, 965 (1978).
3. H. Imoto, J. D. Corbett, *Inorg. Chem.*, **20**, 630 (1981).
4. H. S. Marek, J. D. Corbett, R. L. Daake, *J. Less-Common Met.*, **89**, 243 (1983).
5. A. Simon, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).

Abbreviations

abs	absolute
a.c.	alternating current
Ac	acetyl, CH_3CO
acac	acetylacetonate anion
acacH	acetylacetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
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
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
Ch.	chapter
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-diazabutadiene
DBA	dibenzylideneacetone
d.c.	direct current
DDT	dichlorodiphenyltrichloroethane, 1,1,1'-trichloro-2,2-bis-(4-chlorophenyl)ethane
dec	decomposed

DED	1,1-bis(ethoxycarbonyl)ethene-2,2-dithiolate, [$[(\text{H}_5\text{C}_2\text{OC}(\text{O}))_2\text{C}=\text{CS}_2]^{2-}$
depe	1,2-bis(diphenylphosphino)ethene, $(\text{C}_6\text{H}_5)_2\text{PCH}=\text{CHP}(\text{C}_6\text{H}_5)_2$
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
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, $1,2-(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2$
dppm	bis(diphenylphosphino)methane, $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CH}_2$
dppp	1,3-bis(diphenylphosphino)propane, $1,3-(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2$
dptpe	1,2-bis(di-p-tolylphosphino)ethane, $1,2-(4-\text{CH}_3\text{C}_6\text{H}_4)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_4\text{CH}_3-4)_2$
DTA	differential thermal analysis
DTBQ	3,5-di-t-butyl-o-benzoquinone
DTH	1,6-dithiahexane, butane-1,4-dithiol, $1,4-\text{HS}(\text{CH}_2)_4\text{SH}$
DTS	dithiosquarate
ed.	edition, editor
eds.	editors
EDTA	ethylenediaminetetraacetic acid, $[\text{HOC}(\text{O})]_2\text{N}(\text{CH}_2)_2\text{N}[\text{C}(\text{O})\text{OH}]_2$
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 ₂ O	diethyl ether, (C ₂ H ₅) ₂ O
EtOH	ethanol, C ₂ H ₅ OH
et seq.	et sequentes, and the following
eu	entropy unit
fac	facial
fcc	face-centered cubic
ff.	following
Fig.	figure
Fl	fluorenyl
fp	freezing point
g	gas
g-at	gram-atom
glyme	1,2-dimethoxyethane, CH ₃ O(CH ₂) ₂ OCH ₃
graph	graphite
GS	ground state
h	hour, hours
Hex	hexyl
hmde	hanging mercury drop electrode
HMPA	hexamethylphosphoramide, [(CH ₃) ₂ N] ₃ PO
HOMO	highest occupied molecular orbital
i.e.	id est, that is
Im	imidazole
inter alia	among other things
IR	infrared
irrev	irreversible
ISC	intersystem crossing
isn	isonicotinamide
l	liquid
L	ligand
LC	ligand centered
LF	ligand field
LFER	linear free-energy relationship
liq	liquid
LMCT	ligand-to-metal charge transfer
Ln	lanthanides, rare earths
LSV	linear-scan voltammetry
LUMO	lowest unoccupied molecular orbital
m	meta
max	maximum
M	metal
MC	metal centered
Me	methyl, CH ₃
Men	menthyl
MeOH	methanol, CH ₃ OH
mer	meridional; the repeating unit of an oligomer or polymer
mhp	2-hydroxy-6-methylpyridine, 2-HO, 6-CH ₃ C ₅ H ₃ N
min	minimum, minute, minutes
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
mol	molar
mp	melting point
MV	methyl viologen, 1,1'-dimethyl-4,4'-bipyridinium dichloride
n.a.	not available

napy	naphthyridine
NBD	norbornadiene, [2.2.1]bicyclohepta-2,5-diene
neg	negative
nhe	normal hydrogen electrode
NMR	nuclear magnetic resonance
No.	number
np	tris-[2-(diphenylphosphino)ethyl]amine, $N[CH_2CH_2P(C_6H_5)_2]_3$
Np	naphthyl
NPP	normal pulse polarography
NQR	nuclear quadrupole resonance
NTA	nitilotriacetate
o	ortho
obs	observed
Oct	octyl
OF	oxidation factor
O _n	octahedral
Oq	oxyquinolate
p	para
p.	page
P	pressure
Pat.	patent
pet.	petroleum
Ph	phenyl, C_6H_5
phen	1,10-phenanthroline
Ph ₂ PPy	2-(diphenylphosphino)pyridine, $2-(C_6H_5)_2PC_5H_4N$
pip	piperidine, $C_5H_{10}N$
PMDT	pentamethyldiethylenetriamine, $(CH_3)_2N(CH_2)_2N(CH_3)(CH_2)_2N(CH_3)_2$
PMR	proton magnetic resonance
pn	propylene-1,3-diamine, $1,3-H_2NCH_2CH_2CH_2NH_2$
pos	positive
pp.	pages
ppb	parts per billion
ppm	parts per million
ppn	bis(diphenylphosphino)amine, $[(C_6H_5)_2P]_2NH$
ppt	precipitate
Pr	propyl, C_3H_7
PSS	photostationary state
PVC	poly(vinyl chloride)
PY	pyridine, C_5H_5N
pyr	pyrazine
PZE	potential of zero charge
rac	racemic mixture, racemate
R	organic group; universal gas constant
RDE	rotated disk electrode
RE	rare earths, lanthanides
ref.	reference
rev	reversible
rf	radiofrequency
RF	reduction factor
rh	rhombohedral
rms	root mean square
rpm	revolutions per minute

RT	room temperature
s	second, seconds; solid
sce	saturated calomel electrode
SCE	standard calomel electrode
sec	secondary
Sep	sepulcrate, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane
soln	solution
solv	solvated
sp	specific
STP	standard temperature and pressure
subl	sublimes
Suppl.	supplement
sym	symmetrical, symmetric
t	time; tertiary
T	temperature
T _d	tetrahedral
TCNE	tetracyanoethylene
TEA	tetraethylammonium ion, [(C ₂ H ₅) ₄ N] ⁺
terpy	2,2',2''-terpyridyl
tetraphos	Ph ₂ PCH ₂ CH ₂ PPhCH ₂ CH ₂ PPhCH ₂ CH ₂ PPh ₂
TGA	thermogravimetric analysis
THF	tetrahydrofuran
THP	tetrahydropyran
THT	tetrahydrothiophene
TLC	thin-layer chromatography
TMED	N,N,N',N'-tetramethylethylenediamine, (CH ₃) ₂ N(CH ₂) ₂ N(CH ₃) ₂
TMPPH	2,2,6,6-tetramethylpiperidine, 2,2,6,6-(CH ₃) ₄ C ₅ H ₆ N
Tos	tosyl, tolylsulfonyl, 4-CH ₃ C ₆ H ₄ SO ₂
TPA	tetraphenylarsonium ion, [(C ₆ H ₅) ₄ As] ⁺
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

The entries of this index were derived directly by computer program from the lists of references. The accuracy of the references was the sole responsibility of the authors. No editorial check, except for format and journal title abbreviation, was applied. Consequently, errors occurring in authors' names in the references will recur in this index.

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Compound Index

This index lists individual, fully specified compositions of matter that are mentioned in the text. It is an index of empirical formulas, ordered according to the following system: the elements within a given formula occur in alphabetical sequence except for C, or C and H if present, which always come first. The formulas are ordered alphanumerically without exception.

The index is augmented by successively permuted versions of all empirical formulas. As an example, $C_3H_3AlO_9$ will appear as such and, at the appropriate positions in the alphanumeric sequence, as $H_3AlO_9 * C_3$, $AlO_9 * C_3H_3$ and $O_9 * C_3H_3Al$. The asterisk identifies a permuted formula and allows the original formula to be reconstructed by shifting to the front the elements that follow the asterisk.

Whenever an empirical formula does not show how the elements are combined in groups, it is followed by a linearized structural formula, which reveals the connectivity of the compound(s) underlying the empirical formula and serves to distinguish substances which are identical in composition but differ in the arrangement of elements.

The nonpermuted empirical formulas are followed by keywords. They describe the context in which the compounds represented by the empirical formulas are discussed. Section numbers direct the reader to relevant positions in the book.

AcCl₃

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AcH₂

Formation: 1.12.4.2

AcH₃O₃

Ac(OH)₃

Formation of AcCl₃: 1.12.4.2

Ag

Oxidative addition of methane: 1.10.5.3

Ag[AlH₄]

Formation and decomposition: 1.9.5.1

Ag[BH₄]

Formation and decomposition: 1.9.5.1

AgBO₂*C₂H₆

AgBO₂P₃*C₄₂H₄₇

AgBO₂P₃*C₅₆H₅₁

AgB₃P₂*C₃₆H₃₈

AgB₃P₃*C₅₄H₅₃

Ag[GaH₄]

Formation and decomposition: 1.9.5.1

AgH

Formation: 1.9.2

AgPd

Pd-Ag

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Ag₂*C₂

Ag₂Ca

CaAg₂

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Ag₂CaHCaAg₂H

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Formation: 1.7.2

AlCuH₄CuAlH₄

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AlH₄*Ag**AlH₄K**K[AlH₄]

Formation: 1.7.4.2

AlH₄LiLi[AlH₄]Cleavage of (C₂H₅)₃GeP(C₆H₅)₂:

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 Reduction of $(\text{CH}_3)_3\text{SnCH}_2\text{P}(\text{O})(\text{BH}_3)^*$
 $(\text{OC}_2\text{H}_5)_2$: 1.5.5.2.2
 Reduction of $(\text{CH}_3)_3\text{SnBr}$: 1.6.5.4.1
 Reduction of CH_3SnCl_3 : 1.6.5.4.1
 Reduction of $(n\text{-C}_4\text{H}_9\text{SnCl})_2$: 1.6.5.4.1
 Reduction of R_2SnX_2 : 1.6.5.4.1
 Reduction of R_3SnX : 1.6.6.4
 Reduction of CO_2 : 1.6.5.1.2
 Reduction of $\text{C}_6\text{H}_5\text{CO}_2\text{H}$: 1.6.5.1.2
 Reduction of MgBr -bonded imines:
 1.5.5.1
 Reduction of $\text{C}_2\text{H}_5\text{Br}$: 1.6.5.1.1
 Reduction of $\text{C}_6\text{H}_5\text{C}\equiv\text{CCl}$: 1.6.5.1.4
 Reduction of amides: 1.6.5.1.3
 Reduction of secondary arsines: 1.5.5.3.1
 Reduction of halogermanes: 1.6.5.3.1
 Reduction of alkyllead halides: 1.6.5.5
 Reduction of nitriles: 1.6.5.1.3
 Reduction of organophosphorus acids:
 1.5.5.2.2
 Reduction of organophosphorus esters:
 1.5.5.2.2

AlH₄Li *cont.*

Reduction of phosphinic acids: 1.5.5.2.2

Reduction of diphosphine disulfides:

1.5.5.2.3

Reduction of phosphonate esters:

1.5.5.2.2

Reduction of phosphonous acids:

1.5.5.2.2

Reduction of silanes: 1.6.5.2.1

Reduction of alkoxystannanes: 1.6.5.4.2

Reduction of halostannanes: 1.6.5.4.1

Reduction of chlorostibines: 1.5.5.4

Reduction of dialkylstibines: 1.5.5.4

Reduction of monoalkylstibine: 1.5.5.4

AlH₄NaNaAlH₄

Formation: 1.7.2

Industrial preparation: 1.7.6

AlLi*C₄H₁₂AlLiO*CH₄AlLiO₃*C₁₂H₂₈AlLiO₄*C₂H₄AlLiO₄*C₄H₁₂AlLiO₈*C₄H₄AlLiSi*C₁₈H₁₈AlLiZn*C₂H₁₀AlLiZn₂*C₄H₁₆AlNa*C₆H₁₆AlNaO*C₂H₈AlO*C₁₈H₂₁**AlP**Reaction with D₂O: 1.5.7.1.2Reaction with H₂SO₄: 1.5.3.2.1Al₂*C₆H₁₈Al₂CaCaAl₂Reaction with H₂: 1.12.8.1.2Al₂O₈P₈Ta₂*C₃₆H₉₆Al₃GaH₁₂Ga(AlH₄)₃

Decomposition: 1.7.5.2

Formation: 1.7.5.2

Al₃H₁₂InIn(AlH₄)₃

Formation: 1.7.5.2

Al₃P₂Hydrolysis to yield PH₃ or PD₃: 1.5.6.2Al₄*C₃Al₄*C₃**As**Reaction with H₂O: 1.5.3.3.1Reaction with H₂: 1.5.2.3As*CH₅As*C₂H₇As*C₄H₁₁As*C₆H₇As*C₆H₁₅As*C₇H₉As*C₈H₁₁As*C₈H₁₉As*C₁₂H₁₁As*C₁₂H₂₃As*C₁₄H₁₅As*C₁₈H₁₅AsCl*CH₄AsCl*C₁₃H₁₀AsCl₂*CH₃AsCl₂*C₁₃H₁₁AsCl₂*C₁₈H₁₇AsCl₃Reaction with C₆H₆ to form phenylarsines: 1.5.6.3Reduction by LiBH₄: 1.5.5.3.1AsCrF₆PO₅*C₉H₆AsCrO₅*C₇H₇AsDH₂

Formation: 1.6.7.1.3

AsD₃

Formation: 1.5.7.2.3, 1.6.7.1.3

AsF₃*CH₂AsF₃H₂SiF₃SiAsH₂

Cleavage by protonic acids: 1.5.3.3.3

AsF₃I₂*CAsF₃P₂*CH₄AsF₃Si*C₂H₆AsF₆*C₂HAsF₆*C₆H₇AsF₆I*C₂AsF₆MoO₅PO₅*C₉H₆AsF₉*C₃AsGe*CH₇AsGe*C₃H₁₁AsGe*C₄H₁₃AsGe*C₉H₁₅AsGeH₅H₃GeAsH₂

Cleavage by protonic acids: 1.5.3.3.3

Formation: 1.5.4.3, 1.6.4.3.3

Reaction with D₂O: 1.6.7.1.3Redistribution to AsH₃: 1.5.4.3AsGe₃H₉(H₃Ge)₃As

Cleavage by protonic acids: 1.5.3.3.3

AsH₂K

Formation: 1.5.5.3.2

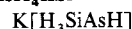
Protonation by H₃SiAsH₂: 1.5.3.3.3**AsH₃**Exchange with acidic D₂O: 1.5.7.2.3

Formation: 1.5.2.3, 1.5.3.3.1, 1.5.3.3.2,

1.5.3.3.3, 1.5.5.3.2

Industrial synthesis by electrochemical reduction: 1.5.6.3

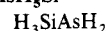
Reaction in silent electric discharge: 1.5.4.3

Reaction with GeH₄: 1.5.4.3.3, 1.6.4.3.3Reaction with SiH₄: 1.5.4.3, 1.6.4.2.3**AsH₄KSi**

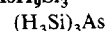
Formation: 1.5.3.3.3

AsH₄P

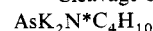
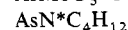
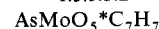
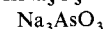
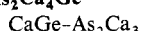
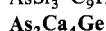
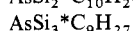
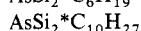
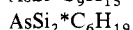
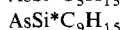
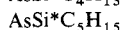
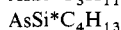
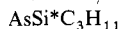
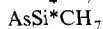
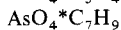
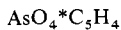
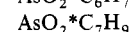
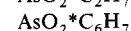
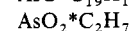
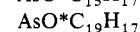
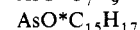
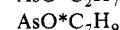
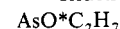
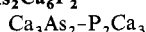
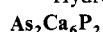
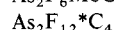
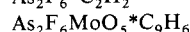
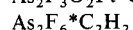
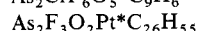
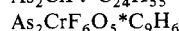
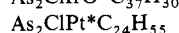
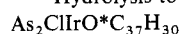
Formation: 1.5.3.2.1

AsH₅Si

Formation: 1.5.4.3, 1.6.4.2.3

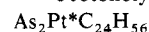
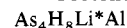
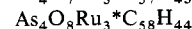
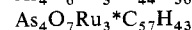
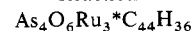
Protonation of KAsH₂: 1.5.3.3.3Reaction with D₂O: 1.6.7.1.3Redistribution to AsH₃: 1.5.4.3**AsH₉Si₃**

Cleavage by protonic acids: 1.5.3.3.3

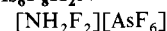
**AsK₃**Protonation by NH₄Br in liq NH₃: 1.5.3.3.2**AsNa₃**Hydrolysis to AsH₃: 1.5.3.3.1, 1.5.3.3.3Protonation by NH₄Br in liq NH₃: 1.5.3.3.2Reaction with D₂O: 1.6.7.1.3**AsNa₃O₃**Reaction with CHO₂Na: 1.5.4.3Hydrolysis to H₃GeAsH₂: 1.5.3.3.1Hydrolysis to H₂PAsH₂: 1.5.3.2.1**As₂H₄**

Formation: 1.5.3.2.1, 1.5.3.3.1, 1.5.4.3, 1.5.5.3.2

Thermal decomposition: 1.5.5.3.2

As₂Mg₃Protonolysis to AsH₃: 1.5.3.3.1**As₂Zn₃**Protonolysis to AsH₃: 1.5.3.3.1**As₄O₆**Reaction with H₂O: 1.5.3.3.1**As₄O₁₀**

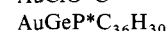
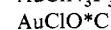
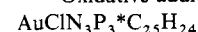
Reaction with elemental hydrogen: 1.5.2.3

Reduction by LiAlH₄: 1.5.5.3.2

Formation: 1.5.3.1.2

Au

Oxidative addition of methane: 1.5.3



- AuGeP***C₃₆H₃₁
AuMnO₅P₂*C₂₃H₁₅
Au₂*C₂
BBr₃
 Reduction with HCHO: 1.7.3.2
B*C₆H₉
B*C₆H₁₅
B*C₉H₂₁
BClF₄OP₂Pt*C₁₃H₃₀
BClO₂*C₂H₆
BCl₂H
 HBCl₂
 Formation: 1.7.3.2
BCl₂N*C₇H₈
BCl₃
 Reaction with LiAlH₄: 1.7.5.1
 Reaction with SiCl₄: 1.7.3.2
 Reduction by H₂: 1.7.2
BCl₃H₄InLi
 LiInCl₃(BH₄)
 Decomposition: 1.7.5.2
 Formation: 1.7.5.2
BCl₃OP*C₁₄H₁₅
BCl₃PS*C₁₄H₁₅
BCr₂
 Cr₂B
 Acid hydrolysis: 1.7.3.1
BCuNP₃*C₅₅H₄₈
BCuO₂P₂*C₂₆H₂₆
BCuO₂P₃*C₅₆H₅₁
BCuP₂*C₂₆H₂₈
BCuP₂*C₃₆H₃₄
BCuP₃*C₂₄H₃₇
BDLi*C₆H₁₅
BD₃*C₉H₁₈
BD₄Li
 LiBD₄
 Reduction of SbCl₃: 1.5.7.1.4
 Reduction of chloroarsines: 1.6.7.1.3
BD₄Na
 Na[BD₄]
 Formation: 1.7.7.2
 Reduction of (CH₃)₂CHBr: 1.6.7.1.1
BF₂H₂Na
 Na[H₂BF₂]
 Formation: 1.7.4.1.1
BF₃
 Reaction with LiAlH₄: 1.7.5.1
 Reduction by LiH: 1.7.4.1.1
BF₃HNa
 Na[HBf₃]
 Formation: 1.7.4.1.1
BF₄FeN₅*C₂₅H₄₆
BF₄FeO₂P*C₂₆H₄₂
BF₄H
 H[BF₄]
 Acid for protonolysis of metal complexes: 1.5.3.1.1
 Protonation of [Ru₂(CO)₃(h⁵-C₅H₅)₂C₃H₄-h³]: 1.6.3.1.3
BF₄IMoN₂P₄*C₅₃H₅₂
BF₄IrN₂P₂*C₄₀H₃₈
BF₄IrO₂*C₁₂H₁₆
BF₄IrO₂P₂*C₃₆H₃₆
BF₄IrO₂P₂*C₃₈H₄₀
BF₄IrO₂P₂*C₄₀H₄₄
BF₄IrO₂P₂*C₄₂H₄₄
BF₄IrO₂P₂*C₄₂H₄₈
BF₄IrO₂P₂*C₄₄H₄₈
BF₄IrO₂P₂*C₄₄H₅₂
BF₄IrP₂*C₄₄H₄₂
BF₄Li
 LiBF₄
 Formation: 1.7.4.1.1
BF₄MnO₆*C₆
BF₄MoN₃O₃*C₉H₁₆
BF₄N*C₃H₁₀
BF₄NO₃P*C₆H₁₃
BF₄N₂O₂Re*C₁₄H₁₂
BF₄N₂O₂Re*C₁₅H₁₆
BF₄OPPt*C₁₇H₃₈
BF₄OP₂Pt*C₁₉H₃₉
BF₄OP₂Pt*C₂₂H₂₆
BF₄O₃Rh₂*C₂₃H₃₁
BF₄O₃Ru₂*C₁₆H₁₅
BF₄O₄P₄Rh*C₆₂H₆₄
BF₄O₄P₄Rh*C₆₂H₆₆
BF₄P₄Rh*C₅₄H₅₂
BF₄P₄Rh*C₅₄H₅₄
BF₇N₂O₂Re*C₁₄H₉
BF₁₂O₂Pt₂*C₃₂H₃₁
BFe₄O₁₂*C₁₂H₃
BGa*C₂H₁₀
BGaN*C₃H₁₅
BGeH₆K
 K[H₃GeBH₃]
 Reaction with aq acid: 1.6.3.3.1
BGeK*C₃H₁₂
BH₃(see also B₂H₆)
 Reduction of CH₃CO₂H: 1.6.4.1.2
 Reduction of C₂H₅CO₂CH₃: 1.6.4.1.2
 Reduction of C₆H₅CN: 1.6.4.1.3
 Reduction of formyl metal complexes: 1.6.4.1.2

- BH₃O₃**
 B(OH)₃
 Reduction with H₂ and Al metal: 1.7.2
- BH₄*Ag**
- BH₄K**
 K[BH₄]
 Reduction of [As(OH)₄]⁻: 1.5.5.3.2
 Reduction of Na₂GeO₃: 1.6.5.3.2
 Reduction of [Sb(OH)₄]⁻: 1.5.5.4
 Reduction of alkyllead halides: 1.6.5.5
- BH₄Li**
 Li[BH₄]
 Formation: 1.7.4.1.1, 1.7.4.1.2
 Reaction with CO₂: 1.6.5.1.2
 Reduction of AsCl₃: 1.5.5.3.1
 Reduction of PCl₃: 1.5.5.2.1
 Reduction of PCl₅: 1.5.5.2.1
 Reduction of SbCl₃: 1.5.5.4
 Reduction of (CH₃)₂NSi(CH₃)₂Cl: 1.6.5.2.3
 Reduction of (C₂H₅O)₂SiHCl: 1.6.5.2.1
 Reduction of (CH₃O)₂SiHCl: 1.6.5.2.2
 Reduction of SiCl₄: 1.6.5.2.1
 Reduction of chloroarsines: 1.5.5.3.1
 Reduction of silazanes: 1.6.5.2.3
- BH₄Na**
 Na[BH₄]
 Formation: 1.7.2, 1.7.4.1.2, 1.7.4.1.3
 Industrial preparation from B(OCH₃)₃: 1.7.6
 Industrial preparation from Na₂B₄*O₇·10H₂O: 1.7.6
 Reaction with BF₃: 1.7.5.1
 Reaction with CO₂: 1.6.5.1.2
 Reduction of [As(OH)₄]⁻ to form AsH₃: 1.5.6.3
 Reduction of [h⁵-C₅H₅Fe(CO)₂CH₂C*HCH₃-h²]⁺: 1.6.5.1.4
 Reduction of [h⁵-C₅H₅(CO)₂Fe]₂Ge*Cl₂: 1.6.5.3.1
 Reduction of (CH₃)₃GeBr: 1.6.5.3.1
 Reduction of CH₃GeBr₃: 1.6.5.3.1
 Reduction of GeCl₄: 1.6.5.3.1
 Reduction of MoBr(NBu-t)₂C₄H₉[(C₆*H₅)₂PCH₂CH₂P(C₆H₅)₂]₂: 1.5.5.1
 Reduction of [h⁵-C₅H₅Re(CO)₂N₂-p-CH₃C₆H₄]₂BF₄: 1.5.5.1
 Reduction of [h⁵-C₅H₅Re(CO)₂N₂-o-CF₃C₆H₄]₂BF₄: 1.5.5.1
 Reduction of [h⁵-C₅H₅Re(CO)₂(NO)]⁺: 1.6.5.1.2
- Reduction of [Sb(OH)₄]⁻ to form SbH₃: 1.5.6.4
 Reduction of (CH₃)₂SbBr: 1.5.5.4
 Reduction of K[CH₃SnO₂]: 1.6.5.4.2
 Reduction of (n-C₄H₉)₃SnCl: 1.6.5.4.1
 Reduction of (C₆H₅)₃SnCl: 1.6.5.4.1
 Reduction of SnCl₂: 1.6.5.4.1
 Reduction of C₆H₅SnCl₃: 1.6.5.4.2
 Reduction of WBr₃[N₂C(CH₃)₂][P(C*H₃)₂C₆H₅]: 1.5.5.1
 Reduction of (CH₃)₂CHBr: 1.6.5.1.1
 Reduction of (C₂H₅)₂CO: 1.6.5.1.2
 Reduction of alkenes: 1.6.5.1.4
 Reduction of nitriles in presence of Mo salts: 1.6.5.1.3
- BH₄Na*Al**
- BH₄Tl**
 Tl[BH₄]
 Decomposition: 1.7.5.2
- BH₆N**
 H₃NBH₃
 Reaction with aq acid: 1.6.3.3.1
- BrP₄*C₆₄H₈₂**
- BK*C₃H₁₀**
- BK*C₁₂H₂₈**
- BK*C₁₈H₁₆**
- BKO₃*C₉H₂₂**
- BLi*C₆H₁₆**
- BLiO₃*C₃H₁₀**
- BLiO₄*C₂H₄**
- BLiO₅*C₄H₁₀**
- BN*C₃H₁₂**
- BNNa*CH₃**
- BNO₂P₂V*C₄₃H₃₉**
- BN₂*C₄H₁₃**
- BN₂Sn*C₁₀H₂₇**
- BN₃*C₂₁H₁₈**
- BNaO₃*C₃H₁₀**
- BNaO₆*C₃H₄**
- BNb*C₁₀H₁₄**
- BO₂*C₂H₆Ag**
- BO₂*C₂H₇**
- BO₂*C₁₈H₁₅**
- BO₂P₃*C₄₂H₄₇Ag**
- BO₂P₃*C₅₆H₅₁Ag**
- BO₂Rh*C₁₈H₂₀**
- BO₃*C₃H₉**
- BO₃*C₃H₁₀**
- BO₃*C₉H₂₁**
- BO₃*C₁₈H₁₅**
- BO₁₂Ru₄*C₁₂H₃**
- BP*C₂H₈**

- BH₆N** *cont.*
BP*C₂H₁₀
BP*C₁₈H₁₈
BPSi*C₅H₁₈
BP₃Pd*C₄₂H₆₆
BPb*C₃H₁₃
BPb*C₆H₁₉
BPb*C₉H₂₅
BPb*C₁₂H₃₁
BZn*CH₇
BZr*C₅H₁₀
B₂BeH₈
 Be(BH₄)₂
 Reaction with (C₆H₅)₃P: 1.8.3.1
B₂BrH₅
 B₂H₅Br
 Reduction with (CH₃)₂SbH: 1.7.3.2
B₂*CH₈
B₂CaH₈
 Ca[BH₄]₂
 Formation: 1.7.4.1.2
B₂CdH₈
 Cd(BH₄)₂
 Formation: 1.9.5.2
B₂ClH₅
 B₂H₅Cl
 Formation: 1.7.2
B₂ClH₈Tl
 TlCl[BH₄]₂
 Formation: 1.7.5.2
B₂Cl₄
 Conversion to B₂H₆ with H₂: 1.7.2
B₂CoF₈P₃*C₁₄H₃₂
B₂CuN₂P₂*C₃₈H₃₆
B₂Cu₂F₄P₄*C₇₂H₆₄
B₂D₆
 Exchange reactions with other boranes: 1.7.7.1
 Formation: 1.7.7.2
 Reduction of CH₃CH=CH₂: 1.6.7.1.1
B₂F₈FeN₅O*C₂₅H₄₇
B₂Fe₂O₆*C₆H₆
B₂GaH₉
 HGa(BH₄)₂
 Formation from HGaCl₂: 1.7.5.2
 Formation from Ga₂Cl₆: 1.7.5.2
B₂H₆ (see also BH₃)
 Exchange with B₂D₆: 1.7.7.1
 Exchange with D₂: 1.7.7.1
 Formation: 1.7.2, 1.7.3.1, 1.7.3.2, 1.7.4.1.1, 1.7.5.1
 Reaction with Pb(C₂H₃)₄: 1.6.4.5.3
 Reaction with SiCl₄: 1.6.4.2.1
 Reaction with (SiH₃)₂O: 1.6.4.2.2
 Reaction with N₂F₄: 1.5.4.1.2
 Reaction with C₂H₄: 1.6.6.1
 Reaction with alkoxyplumbanes: 1.6.4.5.2
 Reduction of C₆H₅CH₂Br: 1.6.4.1.1
 Reduction of CH₃CH=CH₂: 1.6.4.1.4
 Reduction of (CH₃)₂CO: 1.6.4.1.2
 Reduction of alkoxyastannanes: 1.6.4.4.2
 Reduction of aminostannanes: 1.6.4.4.3
B₂H₇Li
 Li[B₂H₇]
 Formation: 1.7.5.1
B₂H₇Na
 Na[B₂H₇]
 Formation: 1.7.5.1
B₂H₈Zn
 Zn[BH₄]₂
 Formation: 1.9.5.2
B₂Li*C₆H₁₉
B₂Mg
 MgB₂
 Base hydrolysis: 1.7.3.1
B₂Mg₃
 Mg₃B₂
 Acidolysis: 1.7.3.1
 Composition: 1.7.3.1
 Reaction with H₂: 1.7.2
B₂O₂
 Hydrogenolysis: 1.7.2
B₂O₃
 Conversion to B₂O₂ by reaction with boron: 1.7.2
 Reduction with LiH: 1.7.4.1.2
 Reduction with Mg: 1.7.3.1
 Reduction with H₂: 1.7.2
 Reduction with carbon: 1.7.2
B₂P₂*C₄H₁₈
B₂Zr*C₅H₁₃
B₂Zr*C₁₀H₁₈
B₃CuH₈
 CuB₃H₈
 Formation as solvate: 1.9.5.1
B₃CuP*C₁₈H₂₃
B₃CuP₂*C₃₆H₃₈
B₃GaH₁₂
 Ga(BH₄)₃
 Formation: 1.7.5.2
B₃H₃O₃
 Disproportionation: 1.7.2
 Formation: 1.7.2
B₃H₃S₆
 (HSBS)₃
 Formation: 1.7.2
 Reduction with H₂: 1.7.2

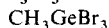
- B₃H₆N₃**
 B₃N₃H₆
 Formation from B-trichloroborazine:
 1.7.5.1
 Reduction to B₃N₃H₁₂: 1.7.5.1
- B₃H₁₂*Al**
B₃H₁₂In
 In(BH₄)₃
 Formation: 1.7.3.2
- B₃H₁₂N₃**
 B₃N₃H₁₂
 Formation: 1.7.5.1
- B₃H₁₂NaZn**
 Na[Zn(BH₄)₃]
 Formation: 1.9.5.2
- B₃IrOP₂*C₃₇H₃₈**
B₃P₂*C₃₆H₃₈Ag
B₃P₃*C₆H₂₄
B₃P₃*C₅₄H₅₃Ag
B₄*C
- B₄CdH₁₆Li₂**
 Li₂Cd(BH₄)₄
 Formation: 1.9.5.2
- B₄DH₉**
 μ-DB₄H₉
 Formation from [B₄H₉]⁻: 1.7.7.2
 Formation from B₅H₁₁: 1.7.7.2
 Intramolecular H-D exchange: 1.7.7.1
- B₄D₂H₈**
 μ-1-D₂B₄H₈
 Formation: 1.7.7.2
- B₄H₉K**
 K[B₄H₉]
 Reaction with B₂H₆: 1.7.5.1
- B₄H₁₀**
 Exchange with B₂D₆: 1.7.7.1
 Formation: 1.7.3.1
 Hydrogenolysis to B₂H₆: 1.7.2
- B₄H₁₆Li₂Zn**
 Li₂Zn(BH₄)₄
 Formation: 1.9.5.2
- B₅*C₂H₇**
B₅*C₂H₁₃
B₅ClH₈
 2-ClB₅H₈
 Reaction with (n-C₄H₉)₃SnD: 1.7.7.2
- B₅CuP₂*C₃₆H₃₈**
B₅DH₈
 μ-DB₅H₈
 Formation: 1.7.7.2
 1-DB₅H₈
 Formation: 1.7.7.2
 Intramolecular H-D exchange: 1.7.7.2
- 2-DB₅H₈
 Formation: 1.7.7.2
- B₅FeO₃*C₃H₉**
B₅H₉
 Electrophilic substitution: 1.7.7.2
 Exchange with D₂: 1.7.7.1
 Exchange with B₂D₆: 1.7.7.1
 Promotion of (SiH₃)₃N disproportionation: 1.6.4.2.3
 Reaction with B₃H₉: 1.6.4.1.4
 Reaction with SiD₄: 1.7.7.1
 Reaction with carbon atoms: 1.6.2.1.1
- B₅H₁₁**
 Formation: 1.7.5.1
 Hydride abstraction from [B₆H₁₁]⁻: 1.7.5.1
- B₅H₁₂K**
 K[B₅H₁₂]
 Formation: 1.7.5.1
- B₆CuP₂*C₃₆H₃₉**
B₆D₄H₈
 1,1,4,4-D₄B₆H₈
 Formation: 1.7.7.1
- B₆H₉K**
 K[B₆H₉]
 Use in higher borane synthesis: 1.7.5.1
- B₆H₁₀**
 Deuteration: 1.7.7.2
 Exchange with B₂D₆: 1.7.7.1
 Formation: 1.7.3.1, 1.7.5.1
 Protonation with HBr: 1.7.3.3
- B₆H₁₁K**
 K[B₆H₁₁]
 Formation: 1.7.5.1
- B₆H₁₂**
 Exchange with B₂D₆: 1.7.7.1
 Formation from [B₆H₁₁]⁻: 1.7.5.1
- B₇H₁₂K**
 K[B₇H₁₂]
 Formation: 1.7.5.1
- B₈H₁₂**
 Reaction with B₂D₆: 1.7.7.1
 Reaction with [B₆H₉]⁻: 1.7.5.1
 Reaction with D₂O: 1.7.7.2
- B₈H₃₂K₂Zn₃**
 K₂[Zn₃(BH₄)₈]
 Formation: 1.9.5.2
- B₉D₃H₁₁K**
 K[4,5,8-D₃B₉H₁₁]
 Formation: 1.7.7.2
- B₉D₈H₉K**
 K[μ-4,6,8-D₃B₉H₉]
 Formation: 1.7.7.2

- B₉H₁₄K**
 K[B₉H₁₄]
 Reaction with D₂O and DCl: 1.7.7.2
- B₉H₁₅**
 Deuteration: 1.7.7.1
- B₁₀Cl₂CuN₂*C₁₆H₅₃**
- B₁₀Cu₂H₁₀**
 Cu₂B₁₀H₁₀
 Formation as solvate: 1.9.5.1
- B₁₀Cu₂P₄*C₇₂H₇₀**
- B₁₀DH₁₃**
 μ-DB₁₀H₁₃
 Formation: 1.7.7.2
- B₁₀D₂H₁₂**
 6,9-D₂B₁₀H₁₂
 Formation: 1.7.7.2
- B₁₀D₄H₄**
 1,2,3,4-D₄B₁₀H₄
 Formation: 1.7.7.2
- B₁₀D₄H₁₀**
 μ-D₄B₁₀H₁₀
 Formation: 1.7.7.2
 5,7,8,10-D₄B₁₀H₁₀
 Formation: 1.7.7.2
- B₁₀D₆H₈**
 2,3,5,7,8,10-D₆B₁₀H₈
 Formation: 1.7.7.2
- B₁₀D₈H₆**
 μ-1,2,3,4-D₈B₁₀H₆
 Formation: 1.7.7.2
 D₈B₁₀H₆
 Formation: 1.7.7.2
 1,2,3,4,5,7,8,10-D₈B₁₀H₆
 Formation: 1.7.7.2
- B₁₀D₁₀H₄**
 μ,5,6,7,8,9,10-D₁₀B₁₀H₄
 Formation: 1.7.7.2
- B₁₀D₁₂H₂**
 μ,1,2,3,4,5,7,8,10-D₁₂B₁₀H₂
 Formation: 1.7.7.2
- B₁₀H₁₃Na**
 Na[B₁₀H₁₃]
 Reaction with DCl: 1.7.7.2
- B₁₀H₁₄**
 B₁₀H₁₄
 Deuteration: 1.7.7.1
 Electrophilic substitution: 1.7.7.2
 Exchange with B₂D₆: 1.7.7.1
 Reaction with DCl in basic solvents: 1.7.7.2
- B₁₀H₁₅N**
 B₁₀H₁₂NH₃
 Formation: 1.5.3.1.1
- B₁₀IrNOP*C₂₉H₃₃**
- B₁₀IrNOP*C₂₉H₃₅**
- B₁₀IrNOP*C₃₄H₃₅**
- B₁₀IrNOP*C₃₄H₃₇**
- B₁₀IrOP₂*C₂₉H₃₇**
- B₁₀IrOP₂*C₂₉H₃₉**
- B₁₀IrOP₂*C₃₀H₃₉**
- B₁₀IrOP₂*C₃₀H₄₁**
- B₁₀IrOP₂*C₃₅H₃₉**
- B₁₀IrOP₂*C₃₅H₄₁**
- B₁₀IrOP₂*C₃₅H₄₃**
- B₁₀IrOP₂*C₃₉H₄₁**
- B₁₀IrOP₂*C₃₉H₄₃**
- B₁₀IrOP₂*C₄₀H₄₃**
- B₁₀IrOP₂*C₄₀H₄₅**
- B₁₀IrOP₂*C₄₅H₄₅**
- B₁₀IrOP₂*C₄₅H₄₇**
- B₁₀IrOP₂*C₃₉H₄₁**
- B₁₀IrO₂P*C₂₈H₃₂**
- B₁₀IrO₃P*C₂₉H₃₀**
- B₁₀IrO₃P*C₂₉H₃₂**
- B₁₀Li₂*C₂H₁₄**
- B₁₀N*CH₁₅**
- B₁₀N*C₄H₂₁**
- B₁₀NSi₂*C₇H₃₁**
- B₁₀Na*CH₁₃**
- B₁₀O₂*C₂H₈**
- B₁₂CdH₁₈**
 Cd(B₆H₉)₂
 Formation: 1.9.5.2
- B₁₂O₂Zn*C₆H₃₄**
- B₁₄H₂₀**
 Formation: 1.7.5.1
- B₃₀ClIrP₃*C₁₂H₅₁**
- Ba**
 Reaction with H₂: 1.8.3, 1.8.3.3
- BaBr₂**
 Structure: 1.8.3
- BaCl₂**
 Structure: 1.8.3
- BaD₄O₄P₂**
 Ba(D₂PO₂)₂
 Formation: 1.5.7.1.2
- BaH₂**
 Formation: 1.8.3.3
- BaH₂O₄P₂**
 Ba[H₂P₂O₄]
 Formation: 1.5.3.2.1
- BaH₄N₂**
 Ba(NH₂)₂
 Hydrolysis: 1.5.3.1.1, 1.5.3.1.3
- BaH₄O₄P₂**
 Ba(H₂PO₂)₂
 Formation: 1.5.3.2.1

- BaI₂**
Structure: 1.8.3
- Ba₃N₂**
Hydrolysis: 1.5.3.1.1, 1.5.3.1.3
- Be*C₂H₆**
Be*C₈H₁₈
- BeH₂**
Covalent hydride: 1.12.1
Formation: 1.8.3, 1.8.3.1
- BeH₈*B₂**
Be₂*C
Be₂Ti
TiBe₂
Reaction with H₂: 1.12.8.1.2
- Be₃N₂**
Hydrolysis to NH₃: 1.5.3.1.1
- BiBr₂*C₆H₅**
Bi*C₂H₅
Bi*C₂H₇
Bi*C₁₈H₁₅
BiCl*C₂H₆
BiCl*C₁₂H₁₀
BiCl₂*CH₃
BiCl₂*C₁₈H₁₅
BiCl₃
Reduction by Li[AlH₄]: 1.5.5.5
- BiF₉*C₃**
BiGe₃*C₉H₂₇
BiGe₃*C₁₈H₄₅
BiH₃
Formation: 1.5.2.5, 1.5.5.5
- BiH₃**
BiH₃
Formation: 1.5.3.5
- BiSi₃*C₁₈H₄₅**
Bi₂Mg₃
Mg₃Bi₂
Hydrolysis by dil HCl: 1.5.3.5
- Br*C₂H₅**
Br*C₃H₇
Br*C₇H₇
Br*C₈H₁₇
- BrCdH**
(CdHBr)_n
Formation: 1.9.5.2
- BrClN₂P₄W*C₅₃H₅₂**
- BrD**
DBr
Addition to alkenes: 1.6.7.1.1
Exchange with C₆H₆ in liq media: 1.6.7.2.1
- BrF₂P**
PF₂Br
Protonation in strong acid: 1.5.3.2.3
- BrGe*C₃H₉**
BrGe*C₆H₁₅
BrGe*C₁₈H₁₅
BrGeH₃
H₃GeBr
Reduction by Li[AlH₄]: 1.6.5.3.1
- BrH**
HBr
Addition to CH₂CH=CH₂PF₂: 1.5.3.2.3
Addition to nitriles: 1.5.6.1
Protonation of alkali-metal germanides: 1.6.3.3.3
Protonation of amines: 1.5.3.1.2
Reactions with amides: 1.5.3.1.3
Reaction with Ge(OH)₂: 1.6.3.3.1
Reaction with elemental Ge: 1.6.2.3
Reaction with cis-Mo(N₂)₂[P(CH₃)₂]*C₆H₅]₄: 1.5.3.1.2
Reaction with trans-Mo(N₂)₂[(C₆H₅)₂]*PCH₂CH₂P(C₆H₅)₂]₂: 1.5.3.1.3
Reaction with SiF₂: 1.6.3.2.3
Reaction with cis-W(N₂)₂[P(CH₃)₂C₆H₅]₄: 1.5.3.1.2
Reaction with CH₃CH=CH₂ in presence of peroxide: 1.6.6.1
- BrH₂N**
H₂NBr
Formation: 1.5.3.1.2
- BrH₃Zn₂**
(Zn₂H₃Br)_n
Formation: 1.9.5.2
- BrH₄N**
[NH₄]Br
Formation: 1.5.3.1.1
Protonation of arsenides in liq NH₃: 1.5.3.3.2
Protonation of [(C₆H₅)₃Ge]Li: 1.6.3.3.2
Protonation of Na[GeH₃] in liq NH₃: 1.6.3.3.2
Protonation of Mg-Si alloys: 1.6.3.2.2
Protonation of Mg₂Sn: 1.6.3.4.2
Reaction with alkylplumbides in liq NH₃: 1.6.3.5
Reaction with organostannides: 1.6.3.4.2
- BrH₄P**
[PH₄]Br
Formation: 1.5.3.2.3
- BrH₅*B₂**
BrIrOP₂*C₁₉H₄₂
BrIrOP₂*C₃₇H₃₀
BrIrOP₂*C₃₇H₆₆
BrIrO₇P₂*C₃₇H₃₀
BrIrP₂*C₂₁H₄₆

- BrMg***C₂H₅
BrMg*C₄H₉
BrMg*C₆H₁₁
BrMgSi*C₁₈H₁₅
BrMoN₂P₄*C₅₆H₅₇
BrNO₂*C₄H₄
BrNP*C₁₈H₁₅
BrNP*C₁₈H₁₇
BrN₂P₄W*C₅₂H₅₁
BrNiP*C₂₁H₂₀
BrO₃Re*C₆H₄
BrP₂Pt*C₁₂H₃₁
BrSb*C₇H₆
BrSb*C₄H₁₀
BrSn*C₃H₉
BrSn*C₄H₁₁
BrSn*C₁₂H₁₁
BrZr
 ZrBr
 Reaction with H₂: 1.12.8.2.4
Br₂
 Reaction with (C₆H₅)₃PNH: 1.5.3.1.3
Br₂*Ba
Br₂*C₆H₅Bi
Br₂ClN₂P₃W*C₂₄H₃₆
Br₂D₂*C₈H₆
Br₂FP
 PFBr₂
 Protonation in strong acid: 1.5.3.2.3
Br₂F₄Si₂
 BrF₂Si₂F₂Br
 Formation: 1.6.3.2.3
Br₂Ge*C₁₂H₁₀
Br₂GeH₂
 H₂GeBr₂
 Reduction by LiAlH₄: 1.6.5.3.1
Br₂Mg
 MgBr₂
 Formation: 1.8.3.2
Br₂MoNP₄*C₅₂H₄₉
Br₂MoN₂P₃*C₂₄H₃₅
Br₂MoN₂P₄*C₅₂H₅₀
Br₂N₂P₃W*C₂₄H₃₅
Br₂N₂P₃W*C₂₇H₃₉
Br₂N₂P₄W*C₅₂H₅₀
Br₂Sr
 SrBr₂
 Structure: 1.8.3
Br₂Zn
 ZnBr₂
 Reduction by LiH to ZnH₂: 1.9.4.1
Br₃*Al
Br₃*B
- Br₃Fe**
 FeBr₃
 Catalyst in DBr exchange with C₆H₆:
 1.6.7.2.1
Br₃Ge*CH₃
Br₃Ge*C₅H₁₁
Br₃GeH
 HGeBr₃
 Formation: 1.6.2.3, 1.6.3.3.1
 Reduction by LiAlH₄: 1.6.5.3.1
Br₃HInLi
 LiInBr₃H
 Formation: 1.7.4.4
Br₃OP
 OPBr₃
 Reaction with LiH: 1.5.4.2.1
Br₃P
 PBr₃
 Hydrolysis: 1.5.3.2.1, 1.5.3.2.3
 Protonation in strong acid: 1.5.3.2.3
 Reaction with LiH: 1.5.4.2.1
 Reaction with LiD: 1.5.7.1.2
Br₄Ni₂*C₅₆H₄₀
Br₄O₃Rh₂*C₁₃H₁₁
Br₄Sn
 SnBr₄
 Reduction by LiAlH₄: 1.6.5.4.1
Br₆Ga₂
 Ga₂Br₆
 Reduction by (CH₃)₃SiH: 1.7.3.2
Br₁₀Si₅
 (SiBr₂)₅
 Reduction by Li[AlH₄]: 1.6.5.2.1
C
 Reaction of atoms with alkanes, silanes,
 boranes and phosphines: 1.6.2.1.1
 Reaction of atoms with H₂O: 1.6.2.1.1
 Reaction of atoms with H₂ at high T:
 1.6.2.1.1
 Reaction with atomic hydrogen: 1.6.2.1.1
CaSF₃I₂
 CF₃AsI₂
 Reaction with HI and Hg: 1.5.3.3.3
 Reduction by Cu–Zn alloy in acid:
 1.5.3.3.1
CAuClO
 (CO)AuCl
 Reaction with [(C₆H₅)₂P]₂N₃P(CH₃)H:
 1.5.3.1.3
CB₄
 B₄C
 Reaction with B₂O₃ at high T: 1.7.2

- Reaction with TiO_2 and H_2 at high T:
1.7.2
- CBe₂**
Be₂C
Hydrolysis: 1.6.2.5
Reaction with protonic acids: 1.6.3.1.3
- CCaN₂**
CaCN₂
Protonation to H_2NCN : 1.5.3.1.1
- CCl₂F₃N**
CF₃NCI₂
Reaction with HCl: 1.5.3.1.3
- CCl₂F₃P**
CF₃PCI₂
Hydrolysis to form $\text{CF}_3\text{PH}(\text{O})\text{OH}$:
1.5.6.2
- CCl₄**
Catalyst for reaction of H_2 with Mg metal: 1.8.3.2
- CD₄**
Formation: 1.6.7.1.1
- CF₃O**
COF₂
Reaction with $\text{CH}_3\text{N}(\text{CHO})_2$: 1.5.4.1.3
- CF₃I₂P**
CF₃PI₂
Reaction with HI and Hg metal:
1.5.3.2.3
- CF₃P**
CF₃PF₂
Reaction with $\text{K}[\text{HF}_2]$: 1.5.3.2.3
- CH**
Formation in gas phase: 1.6.3.1.3
- CHF₃**
CF₃H
Formation: 1.6.2.5, 1.6.4.1.5
- CHF₃KP**
K[CF₃P(H)F₄]
Formation: 1.5.3.2.3
- CHKO**
KHCO
Formation: 1.6.4.1.2
- CHKO₂**
K[O₂CH]
Formation: 1.6.4.1.2
- CHLiO₂**
Li[O₂CH]
Formation: 1.6.4.1.2
- CHN**
HCN
Addition to alkenes: 1.6.6.1
Formation: 1.6.2.1.1, 1.6.3.1.3
Industrial formation: 1.6.6.1
- Oxidative addition: 1.10.5.3
- CHNO**
HNCO
Formation: 1.5.3.1.3
- CHN₃O₆**
(NO₂)₃CH
Formation: 1.6.2.5
- CHNaO₂**
NaCHO₂
Reaction with Na_3AsO_3 : 1.5.4.3
Na[O₂CH]
Formation: 1.6.4.1.2
- CHNaO₃**
NaHCO₃
Reaction with CaH_2 : 1.6.4.1.2
- CHP**
HCP
Formation: 1.6.2.1.1
- CH₂AsF₃**
CF₃AsH₂
Formation: 1.5.3.3.1, 1.5.3.3.3, 1.5.4.3
- CH₂F₃N**
CF₃NH₂
Formation: 1.5.3.1.3
- CH₂F₃O₂P**
CF₃PH(O)OH
Formation: 1.5.3.2.1
Industrial synthesis: 1.5.6.2
- CH₂F₃P**
CF₃PH₂
Formation: 1.5.3.2.1
- CH₂N₂**
H₂NCN
Formation: 1.5.3.1.1
(H₂NCN)_x
Formation: 1.5.4.1.3
- CH₂O**
H₂CO
Formation: 1.6.3.1.3, 1.6.4.1.2, 1.6.4.1.5
- CH₂O₂**
HCO₂H
Reaction with (Cl₃CPN)₂: 1.5.3.1.3
- CH₂Th**
ThCH₂
Formation: 1.12.8.2.2
- CH₃AsCl₂**
Reaction with $\text{C}_2\text{H}_5\text{SbH}_2$: 1.5.4.3
- CH₃BNNa**
Na[BH₃CN]
Reduction of $[\text{h}^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_3]^+$:
1.6.5.1.2
- CH₃BiCl₂**
Reduction by Li[AlH₄]: 1.5.5.5
Reduction by Li[AlD₄]: 1.5.7.2.1

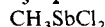
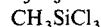
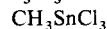
CH₃Br₃GeReduction by Na[BH₄]: 1.6.5.3.1**CH₃Cl**

Reaction with Cu-Si at high T: 1.6.6.2

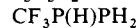
Reaction with elemental Si and H₂:
1.6.2.2**CH₃Cl₂P**Hydrolysis to form CH₃PH(O)OH:
1.5.6.2Reaction with CH₃OH: 1.5.3.2.3

Reaction with LiH: 1.5.4.2.1

Reaction with HF: 1.5.3.2.3

CH₃Cl₂SbReduction by Li[AlH₄]: 1.5.5.4**CH₃Cl₃Ge**Reduction by Li[(t-C₄H₉O)₃AlH]:
1.6.5.3.1Reduction by Li[AlH₄]: 1.6.6.3**CH₃Cl₃Si**Reduction by Li[AlH₄]: 1.6.5.2.1**CH₃Cl₃Sn**Reduction by (C₂H₅)₃AlH: 1.6.4.4.1Reduction with Li[AlH₄]: 1.6.5.4.1**CH₃D**

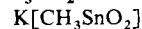
Formation: 1.6.7.1.1

CH₃F₃P₂

Formation: 1.5.4.2.4

CH₃I Zn

Reduction with NaH: 1.9.4.1

CH₃KO₂SnReduction by Na[BH₄]: 1.6.5.4.2**CH₃Li**

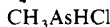
Hydrolysis: 1.6.2.5

CH₄Formation: 1.6.2.1.1, 1.6.2.1.2, 1.6.2.2,
1.6.2.5, 1.6.3.1.3, 1.6.4.1.2, 1.6.4.1.5,
1.6.5.1.2, 1.6.5.1.3, 1.6.6.1Impurity in H₂: 1.8.2

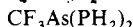
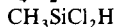
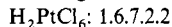
Protonation in gas phase: 1.6.3.1.3

CH₄AlLiO

Formation: 1.6.5.1.2

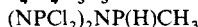
CH₄AsCl

Formation: 1.5.4.3

CH₄AsF₃P₂Decomposition to CF₃AsH₂: 1.5.4.3**CH₄Cl₂Si**Exchange with SiCl₃D in presence of

Formation: 1.6.2.2

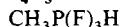
Industrial formation: 1.6.6.2

Reaction with C₆H₅C(CH₃)=CH₂:
1.6.4.1.4**CH₄Cl₄N₃P₃**

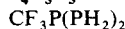
Formation: 1.5.3.2.3

CH₄F₂Ge

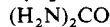
Formation: 1.6.4.3.1

CH₄F₃P

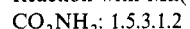
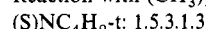
Formation: 1.5.3.2.3

CH₄F₃P₃Disproportionation to (PH)_n and CF₃*
P(H)PH₂: 1.5.4.2.4**CH₄GeO₂**

Disproportionation: 1.6.4.3.3

CH₄N₂OThermolysis to NH₃: 1.5.4.1.3**CH₄N₂O₂**Thermolysis to N₂H₄: 1.5.4.1.3**CH₄O**Cleavage of group-IVB phosphines:
1.5.3.2.3

Formation: 1.6.2.1.2

Formation in CO reaction with H₂ us-
ing a Zn-Cr₂O₃ catalyst: 1.6.6.1Formation in CO reaction with H₂ us-
ing a Pd-Ca₂O₃ catalyst: 1.6.6.1Reaction with Mn(CO)₃[P(C₆H₅)₃]Reaction with Cl₃PNP(O)Cl₂: 1.5.3.1.3Reaction with (CH₃)₃SiN[C(CH₃)₃]P*
(S)C₄H₉-t: 1.5.3.1.3Reaction with (CH₃)₃SiN[Si(CH₃)₃]P*Reaction with [(CH₃)₃Si]₂NC₆H₅:
1.5.3.1.2

- Reaction with $(\text{C}_6\text{H}_5)_3\text{SiSi}(\text{C}_6\text{H}_5)_2\text{CH}_3$:
1.6.4.2.3
Reaction with $(\text{C}_6\text{H}_5)_2\text{SnH}_2$: 1.6.3.4.3
Reaction with $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiN}_2\text{MgCl}$:
1.5.3.1.3
Reaction with $\text{W}_2[\text{N}(\text{CH}_3)_2]_6$: 1.5.3.1.2
Reaction with $(\text{CH}_3)_2\text{Cd}$: 1.6.3.1.3
- CH_4OSi**
 $(\text{CH}_3\text{SiHO})_n$
Reduction of $[(n\text{-C}_4\text{H}_9)_3\text{Sn}]_2\text{O}$: 1.6.6.4
Reduction of stannyl oxides: 1.6.4.4.2
Reaction with $(\text{CH}_3)_2\text{Cd}$: 1.6.3.1.3
- $\text{CH}_4\text{O}_2\text{P}$**
 $\text{CH}_3\text{PO}_2\text{H}$
Formation: 1.5.3.2.3
- CH_4Th_3**
 Th_3CH_4
Formation: 1.12.8.2.2
- CH_4As**
 CH_3AsH_2
Formation: 1.5.4.3
- CH_4Bi**
 CH_3BiH_2
Disproportionation: 1.5.5.5
Formation: 1.5.5.5, 1.5.7.2.1
- CH_4FGe**
 $\text{CH}_3\text{GeH}_2\text{F}$
Disproportionation: 1.6.4.3.1
- CH_5N**
 CH_3NH_2
Formation: 1.5.3.1.3, 1.6.2.1.1
Protonation in H_2O : 1.5.3.1.1
Reaction with P_4 to form
 CH_3PH_2 : 1.5.6.2
Relative basicity: 1.5.3.1.3
- $\text{CH}_5\text{O}_2\text{P}$**
 $\text{CH}_3\text{PH}(\text{O})\text{OH}$
Formation: 1.5.3.2.3
Industrial synthesis: 1.5.6.2
Thermal disproportionation: 1.5.6.2
- CH_5P**
 CH_3PH_2
Formation: 1.5.4.2.4, 1.5.5.2.1, 1.5.5.2.2
Synthesis from $\text{CH}_3\text{PH}(\text{O})\text{OH}$: 1.5.6.2
Synthesis from P_4 with CH_3NH_2 in
presence of carbon: 1.5.6.2
- CH_5Sb**
 CH_3SbH_2
Formation: 1.5.5.4
- CH_6Ge**
 CH_3GeH_3
Formation: 1.6.4.3.1, 1.6.4.3.3, 1.6.5.3.1
Industrial formation: 1.6.6.3
- $\text{CH}_6\text{N}_2\text{O}_2$**
 $[\text{NH}_4][\text{H}_2\text{NCO}_2]$
Thermolysis to NH_3 : 1.5.4.1.3
- CH_6P_2**
 $\text{H}_2\text{C}(\text{PH}_2)_2$
Formation: 1.5.5.2.1
- CH_6Si**
 CH_3SiH_3
Formation: 1.6.5.2.1
Reaction with $[\text{CH}_3\text{Si}]^+$: 1.6.4.2.3
Reaction with Si atoms in matrix: 1.6.2.2
Reaction with Si_2H_6 : 1.6.4.2.3
- CH_6Sn**
 CH_3SnH_3
Formation: 1.6.4.4.1, 1.6.4.4.3, 1.6.5.4.1,
1.6.5.4.2
- CH_7AsGe**
 $\text{CH}_3\text{GeH}_2\text{AsH}_2$
Cleavage by protonic acids: 1.5.3.3.3
- CH_7AsSi**
 $\text{CH}_3\text{SiH}_2\text{AsH}_2$
Cleavage by protonic acids: 1.5.3.3.3
- CH_7BZn**
 CH_3ZnBH_4
Formation: 1.9.5.2
- CH_7GeP**
 $\text{CH}_3\text{Ge}(\text{PH}_2)_2$
Formation: 1.6.4.3.3
- CH_8B_2**
 $\text{CH}_3\text{B}_2\text{H}_5$
Formation: 1.7.3.2
- CH_8GeP_2**
 $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$
Disproportionation: 1.6.4.3.3
- CH_8Si_2**
 $\text{CH}_3\text{Si}_2\text{H}_5$
Formation: 1.6.4.2.3
- $\text{CH}_{13}\text{B}_{10}\text{Na}$**
 $\text{Na}[\text{B}_{10}\text{H}_{12}\text{CH}]$
Formation: 1.6.4.1.3
- $\text{CH}_{15}\text{B}_{10}\text{N}$**
 $\text{B}_{10}\text{H}_{12}\text{CNH}_3$
Formation: 1.5.3.1.3
- $\text{CH}_{44}\text{Cl}_2\text{GeP}_2\text{Pt}$**
 $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{Pt}^+$
 $\text{Cl}_2(\text{H})\text{Ge}(\text{C}_6\text{H}_5)_3$
Thermolysis: 1.6.4.3.3
- CIN**
ICN
Reaction with atomic H: 1.6.2.1.1
- CKN**
KCN
Reaction with $(\text{C}_6\text{H}_5)_3\text{PAuGe}(\text{C}_6\text{H}_5)_3$
in CH_3OH : 1.6.3.3.3

CNNaO

Reaction with protonic acids: 1.5.3.1.3

CNb₂Reaction with H₂: 1.12.8.2.2**CO**

Poisoning of hydriding reaction:

1.12.8.1.1

Reaction with Li[AlH₄]: 1.6.5.1.2Reaction with (h⁵-C₅H₅)₂ZrHCl:

1.6.4.1.2

Reaction with H₂: 1.6.2.1.2Reaction with H₂ and [HRu₃(CO)₁₀]*[Si(C₂H₅)₃]₂⁻: 1.6.2.2Reaction with H₂ and n-C₄H₉CH=C*H₂: 1.6.2.1.2Reaction with H₂ and alkenes: 1.6.6.1Reaction with H₂ over catalysts to produce hydrocarbons: 1.6.6.1Reaction with H₂ to form CH₃OH:

1.6.6.1

Reaction with H₂ to produce(CH₂OH)₂: 1.6.6.1Reduction by CaH₂: 1.6.4.1.2

Reduction by KH: 1.6.4.1.2

Surface impurity: 1.12.1

CO₂Electrolytic reduction to [HCO₂]⁻:

1.6.2.5

Reaction with Na[BH₄]: 1.6.5.1.2

Reaction with group-VIA, metal-carbonyl hydrides: 1.6.4.1.2

Reaction with CaH₂: 1.6.4.1.2Reaction with H₂ over Ni: 1.6.2.1.2

Reaction with alkali-metal hydrides:

1.6.4.1.2

Reduction at Hg cathode: 1.6.2.5

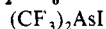
Reduction by Li[BH₄]: 1.6.5.1.2Reduction by CO₂: 1.6.5.1.2**CV₂**Reaction with H₂: 1.12.8.2.2**C₂**

Reactions with hydrogen atoms:

1.6.2.1.1

C₂Ag₂

Hydrolysis: 1.6.2.5

C₂AsF₆I

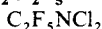
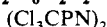
Reaction with HI and Hg: 1.5.3.3.3

Reduction by Cu-Zn alloy in acid:

1.5.3.3.1

C₂Au₂

Hydrolysis: 1.6.2.5

C₂CaN₂Reaction with H₂: 1.5.2.1.2**C₂Cl₂F₄N**Reaction with (CH₃)₃SiH: 1.5.4.1.2**C₂Cl₆N₂P₂**Reaction with HCO₂H: 1.5.3.1.3**C₂Cs₂**

Hydrolysis: 1.6.2.5

C₂Cu₂

Hydrolysis: 1.6.2.5

C₂D₂

Formation: 1.6.7.2.1

C₂D₄

Formation: 1.6.7.2.1

C₂F₄Reaction with h⁵-C₅H₅Fe(CO)₂H:

1.6.4.1.4

C₂F₄Reaction with (CH₃)₂SiH₂: 1.6.4.1.4**C₂F₆**

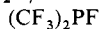
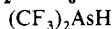
Formation: 1.6.4.1.5

C₂F₆IP

Reaction with HI and Hg: 1.5.3.2.3

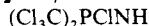
C₂F₆P₂

Formation of d,l- and meso: 1.5.3.2.3

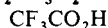
C₂F₇PReaction with K[HF₂]: 1.5.3.2.3**C₂HAsF₆**

Formation: 1.5.3.3.1, 1.5.3.3.3, 1.5.4.3

Thermolysis: 1.6.4.1.5

C₂HCl₇NP

Reaction with HF: 1.5.3.1.3

C₂HF₃O₂Reaction with [h⁵-(CH₃)₅C₅]₂Ni:

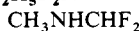
1.6.3.1.3

Reaction with [(CH₃)₃Si]₄N₄: 1.5.3.1.3

- C₂HF₄N**
CF₃CFNH
Formation: 1.5.4.1.2
- C₂HF₆P**
(CF₃)₂PH
Formation: 1.5.3.2.3
Reaction with Fe(CO)₅: 1.10.5.2
Reaction with Fe₃(CO)₁₂: 1.10.5.2
Reaction with (CH₃)₂SiAs(CH₃)₂: 1.5.4.2.3
- C₂HF₆KP**
K[(CF₃)₂P(H)F₃]
Formation: 1.5.3.2.3
- C₂H₂**
Exchange with basic D₂O: 1.6.7.2.1
Formation: 1.6.2.1.1, 1.6.2.5, 1.6.5.1.3, 1.6.6.1
Impurity in H₂: 1.8.2
- C₂H₂As₂F₆**
(CF₃AsH)₂
Formation in d,l- and meso forms: 1.5.3.3.3
- C₂H₂Cl₂FNP**
(CCl₃)₂P(F)CINH₂
Formation: 1.5.3.1.3
- C₂H₂F₆P₂**
(CF₃P)₂H₂
Formation: 1.5.3.2.3
- C₂H₃Cl**
CH₂CHCl
Reaction with (C₆H₅)₃SiH: 1.6.4.1.1, 1.6.7.1.1
- C₂H₃ClO**
CH₃COCli
Reduction by Li[AlH₄]: 1.6.5.1.2
- C₂H₃D**
CH₂CHD
Formation: 1.6.7.1.1
- C₂H₄**
CH₂=CH₂
Dimerization reaction: 1.6.4.1.4
Exchange with D₂SO₄: 1.6.7.2.1
Formation: 1.6.2.1.1, 1.6.2.5, 1.6.3.1.3, 1.6.5.1.1, 1.6.5.1.2
Formation in hydrocarbon cracking: 1.6.6.1
Reaction with Al(BH₄)₃: 1.6.5.1.4
Reaction with B₂H₆: 1.6.6.1
Reaction with PtH(Cl)[P(C₂H₅)₃]₂: 1.6.4.1.4
Reaction with H₂O in presence of [Pd*Cl₄]²⁻-CuCl₂: 1.6.6.1
- Reaction with HCN: 1.6.6.1
- C₂H₄AlLiO₄**
LiAl(OCH₂O)₂
Formation: 1.6.5.1.2
- C₂H₄BLiO₄**
LiBO(OCH₃)O₂CH
Formation: 1.6.5.1.2
- C₂H₄Cl₄Si**
CH₃CHClSiCl₃
Reduction by LiH: 1.6.4.2.1
- C₂H₄N₂O₆S**
O₂S(NHCO₂H)₂
Thermolysis to O₂S(NH₂)₂: 1.5.4.1.3
- C₂H₄O**
CH₃CHO
Industrial formation: 1.6.6.1
- C₂H₄O₂**
CH₃CO₂H
Reaction with BH₃ in THF: 1.6.4.1.2
Reaction with [(C₂H₅)₃Ge]₂Cd: 1.6.3.3.3
- C₂H₅Br**
Reduction by Li[AlD₄]: 1.6.7.1.1
Reduction by Zn: 1.6.2.5
Reduction with Li[AlH₄]: 1.6.5.1.1
- C₂H₅BrMg**
C₂H₅MgBr
Pyrolysis to MgH₂: 1.8.3.2
- C₂H₅ClMg**
C₂H₅MgCl
Reaction with (n-C₄H₉)₃SnH and D₂O: 1.6.7.1.4
- C₂H₅Cl₂P**
C₂H₅PCl₂
Hydrolysis to form C₂H₅PH(O)OH: 1.5.6.2
Reaction with HF: 1.5.3.2.3
- C₂H₅Cl₂Sb**
C₂H₅SbCl₂
Reduction by Li[AlH₄]: 1.5.5.4
- C₂H₅Cl₃Ge**
C₂H₅GeCl₃
Reduction with Li[AlH₄]: 1.6.5.3.1
- C₂H₅Cl₃Si**
C₂H₅SiCl₃
Reduction by Li[AlH₄]: 1.6.5.2.1
- C₂H₅Cl₃Sn**
C₂H₅SnCl₃
Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
- C₂H₅D**
Formation: 1.6.7.1.1

C₂H₅DO

Exchange with h⁶-C₆H₆Cr(CO)₃:
1.6.7.2.1

C₂H₅F₂N

Formation: 1.5.4.1.3

C₂H₅I

Reaction with (C₂H₅)₂GeH₂: 1.6.4.1.1

C₂H₅Li

Hydrolysis: 1.6.2.5

Reaction with D₂O: 1.6.7.1.1

C₂H₅NO₂

Conversion to C₂H₅NH₂ industrially:
1.5.6.1

C₂H₅OTl

Reaction with Li[BH₄]: 1.7.5.2

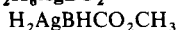
Reaction with B₂H₆: 1.7.3.2

C₂H₆

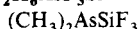
Cracking reaction with H₂: 1.6.2.1.2

Formation: 1.6.2.5, 1.6.3.1.2, 1.6.4.1.1,
1.6.4.1.5, 1.6.5.1.1, 1.6.5.1.2, 1.6.6.1

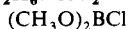
X-Irradiation in presence of Ge₂H₆:
1.6.4.3.3

C₂H₆AgBO₂

Formation: 1.9.5.1

C₂H₆AsF₃Si

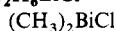
Cleavage by H₂S: 1.5.3.3.3

C₂H₆BClO₂

Reduction by Na[BH₄]: 1.7.5.1

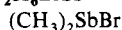
C₂H₆Be

Reaction with Li[AlH₄] to form BeH₂:
1.8.3.1

C₂H₆BiCl

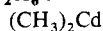
Reduction by Li[AlD₄]: 1.5.7.2.1

Reduction by Li[AlH₄]: 1.5.5.5

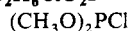
C₂H₆BrSb

Reduction by Li[AlH₄]: 1.5.5.4

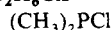
Reduction by Na[BH₄]: 1.5.5.4

C₂H₆Cd

Reaction with CH₃OH: 1.6.3.1.3

C₂H₆ClO₂P

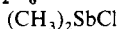
Reduction by (n-C₄H₉)₃SnH: 1.5.4.2.2

C₂H₆CIP

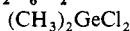
Reaction with CH₃OH: 1.5.3.2.3

Reaction with LiH: 1.5.4.2.1

Reaction with H₂O: 1.5.3.2.3

C₂H₆ClSb

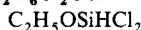
Reduction by Li[AlH₄]: 1.5.5.4

C₂H₆Cl₂Ge

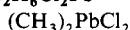
Exchange with germanes: 1.6.4.3.1

Reduction with Li[(t-C₄H₉O)₃AlH]:
1.6.5.3.1

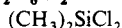
Reduction with Li[AlH₄]: 1.6.5.3.1

C₂H₆Cl₂OSi

Reduction by Li[BH₄]: 1.6.5.2.2

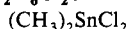
C₂H₆Cl₂Pb

Reduction by Li[AlH₄]: 1.6.5.5

C₂H₆Cl₂Si

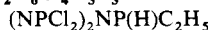
Reduction by Li[AlH₄]: 1.6.5.2.1

Reduction by (C₂H₅)₂AlH: 1.6.4.2.1

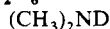
C₂H₆Cl₂Sn

Reduction by Li[AlH₄]: 1.6.5.4.1

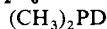
Reduction by (C₂H₅)₂AlH: 1.6.4.4.1

C₂H₆Cl₄N₃P₃

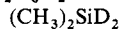
Formation: 1.5.3.2.3

C₂H₆DN

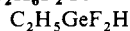
Formation: 1.5.3.1.3

C₂H₆DP

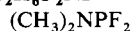
Formation: 1.5.7.1.2

C₂H₆D₂Si

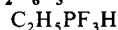
Reagent for trapping divalent phosphorus species: 1.5.4.2.4

C₂H₆F₂Ge

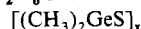
Formation: 1.6.4.3.1

C₂H₆F₂NP

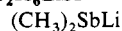
Reaction with K[HF₂]: 1.5.3.2.3

C₂H₆F₃P

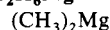
Formation: 1.5.3.2.3

C₂H₆GeS

Reduction by Li[AlH₄]: 1.6.5.3.3

C₂H₆LiSb

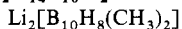
Reaction with H₂O: 1.5.3.4

C₂H₆Mg

Reactions with Li[AlH₄]: 1.8.3.2

- C₂H₆NNa**
Na[(CH₃)₂N]
Reaction with DCl: 1.5.3.1.3
- C₂H₆O**
CH₃CH₂OH
Formation: 1.6.4.1.2, 1.6.5.1.2
Reaction with (C₆H₅)₃PPt(Cl)₂CNC₆*
H₅: 1.5.3.1.2
Reaction with [(CH₃)₂N]₃P: 1.5.3.1.2
Reaction with C₆H₅PCl₂: 1.5.6.2
Reaction with Cl₃PNP(O)Cl₂: 1.5.3.1.3
Reaction with W₂[N(CH₃)₂]₆: 1.5.3.1.2
- C₂H₆O₂**
HOCH₂CH₂OH
Formation in CO-H₂ reaction: 1.6.2.1.2
Industrial formation: 1.6.6.1
- C₂H₆Si**
(CH₃)₂Si
Reaction with CH₃OH: 1.6.3.2.3
Reaction with H₂O: 1.6.3.2.1
Reaction with alcohols: 1.6.3.2.3
Reaction with amines: 1.6.3.2.3
- C₂H₆Sn**
(CH₃)₂Sn
Reaction with HCl or [NH₄][HF₂]:
1.6.3.4.3
- C₂H₆Zn**
(CH₃)₂Zn
Reduction to K[ZnH(CH₃)₂] by KH:
1.9.4.1
- C₂H₇As**
(CH₃)₂AsH
Formation: 1.5.3.3.1, 1.5.3.3.3, 1.5.6.3
Reaction with (CF₃)₄P₂: 1.5.3.2.3
Reaction with CF₃C≡CCF₃: 1.6.4.1.4
- C₂H₇AsO**
(CH₃)₂AsOH
Reduction by Zn in HCl: 1.5.3.3.1
- C₂H₇AsO₂**
(CH₃)₂As(O)OH
Reduction by Zn in HCl: 1.5.3.3.1,
1.5.6.3
- C₂H₇BO₂**
(CH₃O)₂BH
Redistribution: 1.7.5.1
Formation: 1.7.5.1
- C₂H₇B₃**
B₅C₂H₇
Formation: 1.6.2.1.1
- C₂H₇Bi**
(CH₃)₂BiH
Formation: 1.5.5.5, 1.5.7.2.1
- C₂H₇ClGe**
(CH₃)₂GeClH
Formation: 1.6.3.3.3
- (CH₃)₂GeHCl
Formation: 1.6.4.3.1
- C₂H₇ClO₂Si**
SiHCl(OCH₃)₂
Reduction by Li[BH₄]: 1.6.5.2.2
- C₂H₇ClSi**
CH₃CHClSiH₃
Formation: 1.6.4.2.1
(CH₃)₂SiHCl
Formation: 1.6.4.2.3, 1.6.4.3.1
- C₂H₇ClSn**
(CH₃)₂SnHCl
Formation: 1.6.3.4.3
- C₂H₇D₂PSi**
(CH₃)₂SiD₂PHD
Formation from SiH₃PH₂-(CH₃)₂SiD₂
exchange: 1.5.4.2.4
- C₂H₇FGe**
C₂H₅GeH₂F
Redistribution: 1.6.4.3.1
- C₂H₇KZn**
KZnHMe₂
Formation: 1.9.4.2
- C₂H₇N**
(CH₃)₂NH
Formation: 1.5.3.1.2, 1.5.3.1.3, 1.5.4.1.3
Protonation in H₂O: 1.5.3.1.1
Relative basicity: 1.5.3.1.3
- C₂H₅NH₂
Formation: 1.5.3.1.3, 1.5.4.1.3
Industrial synthesis: 1.5.6.1
Reaction with (CH₃)₂AsN(CH₃)₂:
1.5.3.1.3
- C₂H₇OP**
(CH₃)₂P(O)H
Formation: 1.5.3.2.1
- C₂H₇O₂P**
(CH₃O)₂PH
Formation: 1.5.4.2.2
CH₃PH(O)OCH₃
Formation: 1.5.3.2.3
C₂H₅PH(O)OH
Industrial synthesis: 1.5.6.2
Thermal disproportionation: 1.5.6.2
- C₂H₇O₃P**
(CH₃O)₂P(O)H
Formation: 1.5.3.2.2
- C₂H₇P**
(CH₃)₂PH
Cleavage of (CH₃)₂PN(CH₃)₂: 1.5.4.1.3
Formation: 1.5.3.2.3, 1.5.4.2.3, 1.5.5.2.3
Reaction with (CF₃)₄As₂: 1.5.4.3
- C₂H₅PH₂
Formation: 1.5.3.2.3, 1.5.5.2.2, 1.5.6.2

- C₂H₇PS**
 (CH₃)₂P(S)H
 Conversion to (CH₃)₂P(O)H: 1.5.3.2.1
 Formation: 1.5.3.2.1
- C₂H₇PSi**
 CH₃H₂SiPH₂
 Redistribution in presence of
 Li[OC₂H₅]: 1.5.4.2.4
- C₂H₇Sb**
 (CH₃)₂SbH
 Formation: 1.5.5.4
 C₂H₅SbH₂
 Formation: 1.5.5.4
 Reaction with (CH₃)₂AsCl: 1.5.4.3
- C₂H₇Si**
 (CH₃)₃SiH
 Reagent for trapping GeH₂: 1.6.4.3.3
- C₂H₈AlNaO**
 Na[AlH₃OC₂H₅]
 Formation: 1.7.4.2
- C₂H₈BP**
 [BH₂P(CH₃)₂]_x
 Formation: 1.5.4.2.4
- C₂H₈B₁₀O₂**
 B₁₀H₈(CO)₂
 Reaction with Li[AlH₄]: 1.6.5.1.2
- C₂H₈ClP**
 [(CH₃)₂PH₂]₂Cl
 Formation: 1.5.3.2.1
- C₂H₈Ge**
 (CH₃)₂GeH₂
 Exchange with halogermanes: 1.6.4.3.1
 Formation: 1.6.3.3.1, 1.6.4.3.1, 1.6.4.3.3,
 1.6.5.3.1, 1.6.5.3.3
 C₂H₅GeH₃
 Formation: 1.6.4.3.1, 1.6.5.3.1
- C₂H₈N₂**
 H₂C(NH₂)C(NH₂)H₂
 Formation: 1.5.5.1
- C₂H₈OSi**
 C₂H₅OSiH₃
 Formation: 1.6.5.2.2
- C₂H₈O₂Si**
 (CH₃O)₂SiH₂
 Formation: 1.6.5.2.2
- C₂H₈P₂**
 H₂P(CH₂)₂PH₂
 Formation: 1.5.5.2.2
- C₂H₈Pb**
 (CH₃)₂PbH₂
 Formation: 1.6.5.5
- C₂H₈Si**
 (CH₃)₂SiH₂
 Formation: 1.6.4.2.1, 1.6.4.2.2, 1.6.5.2.1,
 1.6.5.2.2, 1.6.5.2.3
- Reaction with Si atoms in matrix: 1.6.2.2
 Reaction with C₂F₄: 1.6.4.1.4
 Reduction of GeCl₄: 1.6.4.3.1
- C₂H₅SiH₃**
 Formation: 1.6.4.2.2, 1.6.5.2.1
- C₂H₈Sn**
 (CH₃)₂SnH₂
 Formation: 1.6.4.4.1, 1.6.4.4.2, 1.6.4.4.3,
 1.6.5.4.1
 Reaction with (n-C₄H₉)₂Sn: 1.6.4.4.3
 C₂H₅SnH₃
 Formation: 1.6.4.4.3
- C₂H₉F₅NP**
 [(CH₃)₂NH₂]₂PF₅H
 Formation: 1.5.3.2.3
- C₂H₉GeP**
 (CH₃)₂Ge(PH₂)H
 Redistribution: 1.6.4.3.3
- C₂H₉NPS₃**
 [(CH₃)₂NH₂]₂[HP(S)₂]₂
 Formation: 1.5.3.2.3
- C₂H₉NaZn₂**
 Na[Zn₂H₃(CH₃)₂]
 Formation and thermolysis: 1.9.4.1,
 1.9.4.2
- C₂H₁₀AlLiZn**
 Li[H₂AlH₂ZnMe₂]
 Formation: 1.9.5.2
- C₂H₁₀BGa**
 (CH₃)₂GaBH₄
 Formation: 1.7.3.2, 1.7.5.2
- C₂H₁₀BP**
 (CH₃)₂PHBH₃
 Formation: 1.5.4.2.4
- C₂H₁₀GeP₂**
 (CH₃)₂Ge(PH₂)₂
 Formation: 1.6.4.3.3
 Redistribution to [(CH₃)₂Ge]₆P₄ and
 PH₃: 1.5.4.2.4
- C₂H₁₀Ge₂**
 C₂H₅Ge₂H₅
 Formation: 1.6.4.3.3
- C₂H₁₀Si₂**
 (CH₃)₂Si₂H₄
 Formation: 1.6.2.2
- C₂H₁₁PSi₂**
 (CH₃SiH₂)₂PH
 Formation: 1.5.4.2.4
- C₂H₁₂Ge₃**
 C₂H₅Ge₃H₇
 Formation: 1.6.4.3.3
- C₂H₁₃B₅**
 B₅H₈C₂H₅
 Formation: 1.6.4.1.4

C₂H₁₄B₁₀Li₂

Formation: 1.6.5.1.2

C₂K₂

Hydrolysis: 1.6.2.5

C₂Li₂

Hydrolysis: 1.6.2.5

C₂Na₂

Hydrolysis: 1.6.2.5

C₂Rb₂

Hydrolysis: 1.6.2.5

C₂Th

Hydrolysis: 1.6.2.5

C₂Zn

Hydrolysis: 1.6.6.1

C₃

Reactions with hydrogen atoms:

1.6.2.1.1

C₃Al₄

Hydrolysis: 1.6.2.5, 1.6.6.1

Reaction with D₂O: 1.6.7.1.1**C₃AsF₉**

Hydrolysis: 1.6.2.5

C₃BiF₉

Hydrolysis: 1.6.2.5

C₃D₈

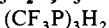
Formation: 1.6.7.2.1

C₃F₉P

Hydrolysis: 1.6.2.5

C₃F₉Sb

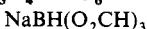
Hydrolysis: 1.6.2.5

C₃H₂F₉P₃

Formation: 1.5.3.2.3

C₃H₄

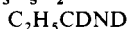
Formation: 1.6.2.5

C₃H₄BNaO₆

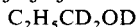
Formation: 1.6.5.1.2

C₃H₅Cl₃Si

Reduction by LiH: 1.6.4.2.1

C₃H₅D₂N

Formation: 1.6.7.1.1

C₃H₅D₃O

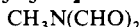
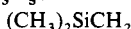
Formation: 1.6.7.1.1

C₃H₅F₂P

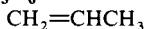
Reaction with HBr: 1.5.3.2.3

C₃H₅N

Industrial formation: 1.6.6.1

Reduction by Li[AID₄]: 1.6.7.1.1**C₃H₅NO₂**Reaction with COF₂: 1.5.4.1.3**C₃H₅NS**Reaction with (C₂H₅)₃SiH: 1.6.4.1.3**C₃H₅Si**

Reaction with protonic acids: 1.6.3.1.3

C₃H₆

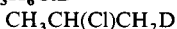
Formation: 1.6.2.1.2, 1.6.5.1.2

Formation in hydrocarbon cracking:

1.6.6.1

Reaction with (C₂H₅)₂AlH: 1.6.6.1Reaction with B₂D₆: 1.6.7.1.1Reaction with B₂H₆: 1.6.4.1.4

Reaction with DCl: 1.6.7.1.1

Reaction with HRh(CO)[P(C₆H₅)₃]₃:
1.6.4.1.4Reaction with (CH₃)₃SiH: 1.6.6.1Reaction with HBr in presence of per-
oxide: 1.6.6.1Reaction with H₂O in presence of acid
catalyst: 1.6.6.1**C₃H₆ClD**

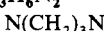
Formation: 1.6.7.1.1

C₃H₆D₂O

Formation: 1.6.7.1.1

C₃H₆F₃P

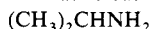
Formation: 1.5.3.2.3

C₃H₆NPReaction with (C₆H₅)₂PCHCH₂:
1.6.4.1.4**C₃H₆N₂**Complexation with AlH₃: 1.7.2

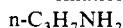
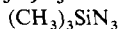
- C₃H₆N₆**
 C₃N₃(NH₂)₃
 Formation: 1.5.4.1.3
- C₃H₆O**
 C₂H₅CHO
 Reaction with AlD₃ in C₄H₈O: 1.6.7.1.1
 Reduction by AlH₃ in THF: 1.6.4.1.2
 (CH₃)₂CO
 Reaction with B₂H₆: 1.6.4.1.2
 Reaction with H₂: 1.6.2.1.2
- C₃H₇Br**
 CH₃CH₂CH₂Br
 Formation: 1.6.6.1
 (CH₃)₂CHBr
 Reduction by Na[BH₄]: 1.6.5.1.1
 Reduction with Na[BD₄]: 1.6.7.1.1
- C₃H₇ClMg**
 (CH₃)CHMgCl
 Conversion of halides to hydrides:
 1.10.8.2
- C₃H₇Cl₂P**
 (CH₃)₂CHPCl₂
 Hydrolysis to form i-C₃H₇PH(O)OH:
 1.5.6.2
- C₃H₇D**
 (CH₃)₂CHD
 Formation: 1.6.7.1.1
- C₃H₇Li**
 LiCH(CH₃)₂
 Hydrolysis: 1.6.2.5
 Reaction with chlorosilanes: 1.6.4.2.1
- C₃H₈**
 (CH₃)₂CH₂
 Exchange with D₂ over Ni film: 1.6.7.2.1
 Exchange with ND₃ in presence of
 [ND₂]⁻: 1.6.7.2.1
 Formation: 1.6.2.5, 1.6.5.1.1, 1.6.5.1.2,
 1.6.6.1
- C₃H₈Cl₄N₃P₃**
 (NPCl₂)₂NP(H)C₃H₇-n
 Formation: 1.5.3.2.3
- C₃H₈O**
 CH₃(CH₂)₂OH
 Formation: 1.6.4.1.2
 Reaction with Cl₃PNP(O)Cl₂: 1.5.3.1.3
 (CH₃)₂CHOH
 Formation: 1.6.2.1.2, 1.6.4.1.2, 1.6.6.1
 Reaction with Mo[N(CH₃)₂]₄: 1.5.3.1.3
 C₂H₅OCH₃
 Formation: 1.6.5.1.2
- C₃H₈O₄S**
 CH₃(CH₂)₂OSO₃H
 Industrial formation: 1.6.6.1
- C₃H₈Si**
 CH₂=CHCH₂SiH₃
 Formation: 1.6.4.2.1
- C₃H₉Al**
 (CH₃)₃Al
 Hydrolysis: 1.6.2.5
 Reaction with D₂O: 1.6.7.1.1
 Reaction with H₂: 1.7.2
- C₃H₉BO₃**
 B(OCH₃)₃
 Reaction with NaH: 1.7.4.1.2
 Reduction to [BH₄]⁻ or NaBH(OC*
 H₃)₃: 1.7.2
 Reduction with LiAlH₄ to BH₃: 1.7.5.1
- C₃H₉B₅FeO₃**
 (CO)₃FeB₅H₉
 Protonation: 1.7.3.3
- C₃H₉BrGe**
 (CH₃)₃GeBr
 Reduction by Zn in H₂O: 1.6.3.3.1
 Reduction with NaBH₄: 1.6.5.3.1
- C₃H₉BrSn**
 (CH₃)₃SnBr
 Reduction by LiAlH₄: 1.6.5.4.1
- C₃H₉ClGe**
 (CH₃)₃GeCl
 Reduction with Li[(t-C₄H₉O)₃AlH]:
 1.6.5.3.1
- C₃H₉ClPb**
 (CH₃)₃PbCl
 Reduction by LiAlH₄: 1.6.5.5
 Reduction with (C₂H₅)₂AlH: 1.6.4.5.1
- C₃H₉ClSi**
 (CH₃)₃SiCl
 Formation: 1.6.3.1.3
 Reaction with CaH₂: 1.6.6.2
 Reduction by Al(BH₄)₃: 1.6.5.2.1
- C₃H₉ClSn**
 (CH₃)₃SnCl
 Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
- C₃H₉D₂NSi**
 (CH₃)₃SiND₂
 Formation from Na[[CH(CH₃)₃Si]₂N]:
 1.5.3.1.3
- C₃H₉Ga**
 (CH₃)₃Ga
 Reaction with B₂H₆: 1.7.3.2
- C₃H₉GeN₃**
 (CH₃)₃GeN₃
 Hydrolysis: 1.5.3.1.3
- C₃H₉In**
 (CH₃)₃In
 Reaction with B₂H₆: 1.7.3.2

C₃H₉N

Relative basicity: 1.5.3.1.3



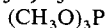
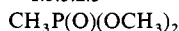
Formation: 1.5.5.1

Reaction with $(\text{CH}_3)_2\text{AsN}(\text{CH}_3)_2$:
1.5.3.1.3**C₃H₉N₃Si**

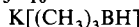
Hydrolysis: 1.5.3.1.3

C₃H₉NaSnReaction with $[\text{NH}_4]\text{Br}$ in liq NH_3 :
1.6.3.4.2**C₃H₉O₂P**

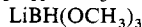
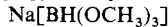
Industrial synthesis: 1.5.6.2

C₃H₉O₃PProtonation in strong acid: 1.5.3.2.2,
1.5.3.2.3Reduction by LiAlH_4 : 1.5.5.2.2**C₃H₁₀BF₄N**

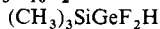
Formation: 1.5.3.1.3

C₃H₁₀BK

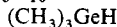
Formation: 1.7.5.1

C₃H₁₀BLiO₃Reduction of $(\text{CH}_3)_2\text{SbBr}$: 1.5.5.4**C₃H₁₀BNaO₃**

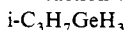
Formation: 1.7.2, 1.7.4.1.2

C₃H₁₀BO₃Reaction with LiH : 1.7.4.1.1**C₃H₁₀F₂GeSi**

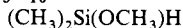
Formation: 1.6.4.3.1

C₃H₁₀GeFormation: 1.6.3.3.1, 1.6.3.3.3, 1.6.4.3.1,
1.6.5.3.1

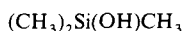
Industrial formation: 1.6.6.3

Reaction with Ge_2H_6 : 1.6.4.3.3

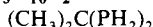
Formation: 1.6.4.3.1

C₃H₁₀OSi

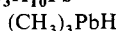
Formation: 1.6.3.2.3



Formation: 1.6.3.1.3

C₃H₁₀P₂

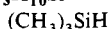
Formation: 1.5.5.2.1

C₃H₁₀Pb

Formation: 1.6.4.5.1, 1.6.4.5.2, 1.6.5.5

Reaction with $\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$: 1.6.4.1.4

Self-association reaction: 1.6.4.5.3

C₃H₁₀SiFormation: 1.6.4.2.2, 1.6.4.2.3, 1.6.5.2.1,
1.6.5.2.3

Industrial formation: 1.6.6.2

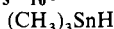
Reaction with Ge atoms: 1.6.2.3

Reaction with PF_5 : 1.5.4.2.3Reaction with Si atoms in a matrix:
1.6.2.2Reaction with $\text{C}_2\text{F}_5\text{NCl}_2$: 1.5.4.1.2Reaction with CH_2CHCH_3 : 1.6.6.1Reaction with $\text{CH}_2\text{CH}=\text{CHCH}_2$:
1.6.4.1.4

Thermolysis: 1.6.4.2.3

C₃H₁₀Si₂

Formation: 1.6.4.2.3

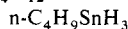
C₃H₁₀SnFormation: 1.6.2.4, 1.6.3.4.2, 1.6.4.4.1,
1.6.4.4.3, 1.6.5.4.1, 1.6.5.4.3Reaction with $(\text{CH}_3)_2\text{AsAs}(\text{CF}_3)_2\text{Cr}(\text{C}^*\text{O})_5$: 1.5.4.3Reaction with $(\text{CH}_3)_2\text{AsAs}(\text{CF}_3)_2\text{Mo}^*(\text{CO})_5$: 1.5.4.3Reaction with $[(\text{C}_2\text{H}_5)_3\text{Ge}]_3\text{Sb}$ or
 $[(\text{C}_2\text{H}_5)_3\text{Ge}]_3\text{Bi}$: 1.6.4.3.3Reaction with $(\text{CH}_3)_3\text{PbN}(\text{C}_2\text{H}_5)_2$:
1.5.4.1.3Reaction with $(\text{CF}_3)_2\text{PAs}(\text{CH}_3)_2\text{Cr}(\text{C}^*\text{O})_5$: 1.5.4.3Reaction with $(\text{CF}_3)_2\text{PAs}(\text{CH}_3)_2\text{Mo}(\text{C}^*\text{O})_5$: 1.5.4.3Reaction with PF_5 : 1.5.4.2.3Reaction with $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2\text{Cr}(\text{C}^*\text{O})_5$: 1.5.3.2.3Reaction with $(\text{CH}_3)_2\text{PP}(\text{CH}_3)_2\text{Cr}(\text{C}^*\text{O})_5$: 1.5.3.2.3Reaction with $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2\text{Mo}(\text{C}^*\text{O})_5$: 1.5.3.2.3Reaction with $(\text{CH}_3)_2\text{PP}(\text{CH}_3)_2\text{Mo}(\text{C}^*\text{O})_5$: 1.5.3.2.3

- C₃H₁₁AsGe**
 (CH₃)₃GeAsH₂
 Cleavage by protonic acids: 1.5.3.3.3
- C₃H₁₁AsSi**
 (CH₃)₃SiAsH₂
 Cleavage by protonic acids: 1.5.3.3.3
- C₃H₁₂BGeK**
 K[H₃GeB(CH₃)₃]
 Reaction with aq acid: 1.6.3.3.1
- C₃H₁₂BN**
 (CH₃)₃NBH₃
 Formation: 1.7.2
 Reaction with HF: 1.5.3.1.3
- C₃H₁₂Si₂**
 CH₃SiH₂CH₂SiH₂CH₃
 Formation: 1.6.4.2.3
 (CH₃)₃Si₂H₃
 Formation: 1.6.2.2
- C₃H₁₃BPb**
 [(CH₃)₃Pb][BH₄]
 Reaction with CH₃OH: 1.6.4.5.2
- C₃H₁₅BGaN**
 (CH₃)₃NGaH₂(BH₄)
 Formation: 1.7.5.2
- C₃Mg₂**
 Mg₂[C₃]
 Hydrolysis: 1.6.2.5
- C₃O₂**
 Reaction with hydrogen atoms: 1.6.2.1.1
- C₄**
 Reaction with hydrogen atoms: 1.6.2.1.1
- C₄As₂F₁₂**
 (CF₃)₄As₂
 Reaction with (CH₃)₂PH: 1.5.4.3
- C₄D₈**
 CD₂CD₂CD₂CD₃
 Formation: 1.6.7.2.1
- C₄F₆**
 CF₃CCCF₃
 Reaction with (CH₃)₂AsH: 1.6.4.1.4
- C₄F₁₂P₄**
 (CF₃P)₄
 Hydrolysis to CF₃P(O)(OH)H: 1.5.3.2.1
 Hydrolysis to CF₃PH₂: 1.5.3.2.1
 Reaction with H₂O: 1.5.3.2.3
- C₄HCoO₄**
 HCo(CO)₄
 Catalysis of CO reaction with H₂:
 1.6.6.1
 Equilibrium acidity: 1.10.6.2.2
 Formation: 1.10.2, 1.10.3.2
- Generation by protonation of a metal anion: 1.10.6.2.1
- C₄HFeKO₄**
 K[HF₂(CO)₄]
 Protonation at metal: 1.10.6.2.1
- C₄HN₃**
 (CN)₃CH
 Formation: 1.6.2.5, 1.6.3.1.3
- C₄H₂FeO₄**
 H₂Fe(CO)₄
 Equilibrium acidity: 1.10.6.2.2
 Generation by protonation of a metal anion: 1.10.6.2.1
- C₄H₂O₄Os**
 H₂Os(CO)₄
 Equilibrium acidity: 1.10.6.2.2
 Formation: 1.10.3.1
 Generation by protonation of a metal anion: 1.10.6.2.1
 Rate of formation by protonation of anion: 1.10.6.2.3
- C₄H₂O₄Ru**
 H₂Ru(CO)₄
 Formation: 1.10.3.2
- C₄H₄**
 Formation: 1.6.2.5
 Formation from C₄ and H₂: 1.6.2.1.1
- C₄H₄AlLiO₈**
 LiAl(O₂CH)₄
 Formation: 1.6.5.1.2
- C₄H₄BrNO₂**
 C(O)CH₂CH₂C(O)NBr
 Reaction with HBr: 1.5.3.1.3
- C₄H₄O**
 Reaction with H₂ over Ni: 1.6.6.1
- C₄H₅NO₂**
 C(O)CH₂CH₂C(O)NH
 Formation: 1.5.3.1.3
- C₄H₆**
 CH₂CH=CHCH₂
 Reaction with (CH₃)₃SiH: 1.6.4.1.4
 CH₃CHC≡CH₂
 Formation from C₄ and hydrogen:
 1.6.2.1.1
 CH₃C≡CCH₃
 Reaction with H₂ over Pd-C: 1.6.2.1.2
 Reaction with Na in liq NH₃: 1.6.3.1.2
 Reaction with H₂ in presence of Pt:
 1.6.6.1
 Reaction with H₂O in presence of acid catalyst: 1.6.6.1

- C₂H₅C≡CH**
 Formation from C₄ and hydrogen:
 1.6.2.1.1
 Formation in hydrocarbon cracking:
 1.6.6.1
- C₄H₆F₆P₂**
 (CH₃)₂PP(CF₃)₂
 Reaction with HCl or H₂O: 1.5.3.2.3
- C₄H₇O₂**
 CH₂CHCHO₂CH₃
 Reaction with (n-C₄H₉)₃GeH: 1.6.4.1.4
- C₄H₈**
 CH₂=CHCH₂CH₃
 Catalyst for exchange of D₂SO₄ with
 CH₂=CHCH₂CH₃: 1.6.7.2.1
 Exchange with D₂SO₄ in CH₃OD in
 presence of [DNi[P(OC₂H₅)₃]₄]⁺:
 1.6.7.2.1
 Formation: 1.6.4.1.4
 Isomerization in presence of Ni: 1.6.6.1
 Thermal isomerization: 1.6.4.1.5
- cis-CH₃CH=CHCH₃
 Formation: 1.6.2.1.2
 Industrial formation: 1.6.6.1
- trans-CH₃CH=CHCH₃
 Formation: 1.6.3.1.2
- CH₃CH=CHCH₃
 Formation: 1.6.6.1
- C₂H₅CH=CH₂
 Formation: 1.6.2.5
 Formation in hydrocarbon cracking:
 1.6.6.1
 Reaction with (CH₃)₃PbH: 1.6.4.1.4
- (CH₃)₂C=CH₂
 Reaction with (CH₃)₃CH in presence of
 H₂SO₄ catalyst: 1.6.6.1
- C₄H₈O**
 CH₃CH₂C(O)CH₃
 Formation: 1.6.6.1
 Industrial formation: 1.6.6.1
- C₄H₈O₂**
 C₂H₅CO₂CH₃
 Reduction by BD₃ in C₄H₈O: 1.6.7.1.1
 Reduction by BH₃ in THF: 1.6.4.1.2
- C₄H₉BrMg**
 n-C₄H₉MgBr
 Hydrolysis: 1.6.2.5
 Reaction with DCl: 1.6.7.1.1
 Reaction with HCl: 1.6.3.1.3
- C₄H₉Cl₂P**
 n-C₄H₉PCl₂
 Reaction with HF: 1.5.3.2.3
- t-C₄H₉PCl₂
 Reaction with HF: 1.5.3.2.3
- C₄H₉Cl₂Sb**
 n-C₄H₉SbCl₂
 Reduction by LiAlH₄: 1.5.5.4
- C₄H₉Cl₃Sn**
 n-C₄H₉SnCl₃
 Reduction by NaBH₄: 1.6.5.4.1
- C₄H₉D**
 n-C₄H₉D
 Formation: 1.6.7.1.1
- C₄H₉Li**
 n-C₄H₉Li
 Hydrolysis: 1.6.2.5
 Reaction with P₂H₄: 1.5.4.2.4
 Reaction with NH₃: 1.6.3.1.2
- t-C₄H₉Li
 Hydrolysis: 1.6.2.5
 Reaction with {[(CH₃)₃Si]₂P}₂PCl:
 1.5.4.2.4
- C₄H₉NO₂**
 n-C₄H₉NO₂
 Industrial conversion to n-C₄H₉NH₂:
 1.5.6.1
- C₄H₁₀**
 i-C₄H₁₀
 Formation: 1.6.2.5
- n-C₄H₁₀
 Cleavage by H₂ over Ni-Cu catalyst:
 1.6.6.1
 Formation: 1.6.2.5, 1.6.2.5, 1.6.3.1.2,
 1.6.3.1.3
- t-C₄H₁₀
 Reaction with (CH₃)₂CCH₂ in presence
 of an H₂SO₄ catalyst: 1.6.6.1
- C₄H₁₀AlD**
 (C₂H₅)₂AlD
 Reduction of halostannanes: 1.6.7.1.4
- C₄H₁₀AsK₂N**
 K₂[n-C₄H₉AsNH]
 Protonation by NH₄Cl in liq NH₃:
 1.5.3.3.2
- C₄H₁₀BLiO₅**
 LiB(OCH₃)₃(O₂CH)
 Formation: 1.6.5.1.2
- C₄H₁₀BrSb**
 (C₂H₅)₂SbBr
 Reduction by LiAlH₄: 1.5.5.4
- C₄H₁₀Cl₂Ge**
 (C₂H₅)₂GeCl₂
 Exchange with germanes: 1.6.4.3.1
 Reduction by LiAlH₄: 1.6.5.3.1

- C₄H₁₀Cl₂O₂Si**
(C₂H₅O)₂SiCl₂
Reduction by NaH: 1.6.4.2.2
- C₄H₁₀Cl₂Pb**
(C₂H₅)₂PbCl₂
Reduction by LiAlH₄: 1.6.5.5
- C₄H₁₀Cl₂Si**
(C₂H₅)₂SiCl₂
Reduction by LiAlH₄: 1.6.6.2
- C₄H₁₀Cl₂Sn**
(C₂H₅)₂SnCl₂
Reduction by LiAlH₄: 1.6.5.4.1
Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
- C₄H₁₀Cl₂Ti**
(C₂H₅)₂TiCl₂
Reaction with NaC₁₀H₇: 1.5.3.1.3
- C₄H₁₀F₂O₂Si**
(C₂H₅O)₂SiF₂
Reduction by NaH: 1.6.4.2.1
- C₄H₁₀F₂Si**
(C₂H₅)₂SiF₂
Reduction with NaH: 1.6.4.2.1
- C₄H₁₀F₃P**
n-C₄H₉P(F)₃H
Formation: 1.5.3.2.3
t-C₄H₉P(F)₃H
Formation: 1.5.3.2.3
- C₄H₁₀Ge**
(CH₃)₃GeH
Formation: 1.6.5.3.1
- C₄H₁₀LiP**
(C₂H₅)₂PLi
Protonation by [(C₂H₅)₂P]₃SiH:
1.5.3.2.3
- C₄H₁₀LiSb**
(C₂H₅)₂SbLi
Reaction with H₂O: 1.5.3.4
- C₄H₁₀Mg**
(C₂H₅)₂Mg
Pyrolysis to MgH₂: 1.8.3.2
- C₄H₁₀N₂O₂Ti**
[Ti(OC₂H₅)₂N₂]_n
Reaction with NaC₁₀H₇: 1.5.3.1.3
- C₄H₁₀N₄Si**
CHN₃NSi(CH₃)₃
Disproportionation to (H₂NCN)_n:
1.5.4.1.3
- C₄H₁₀O**
t-C₄H₉OH
Reaction with silyl azides: 1.5.3.1.3
- C₄H₁₀O₂Ti**
[Ti(OC₂H₅)₂]_x
Reaction with N₂: 1.5.3.1.3
- C₄H₁₀Sn**
(C₂H₅)₂Sn
Reaction with HCl or [NH₄][HF₂]:
1.6.3.4.3
- C₄H₁₀Zn**
Zn(C₂H₅)₂
Reaction with NH₃: 1.6.3.1.2
- C₄H₁₁Al**
(C₂H₅)₂AlH
Reaction with CH₃CH=CH₂: 1.6.6.1
Reduction of (CH₃)₂Si(OC₂H₅)₂:
1.6.4.2.2
Reduction of (CH₃)₂SiCl₂: 1.6.4.2.1
Reduction of (C₂H₅)₃SiF: 1.6.4.2.1
Reduction of (C₂H₅O)₄Sn: 1.6.4.4.2
Reduction of chloroplumbanes: 1.6.4.5.1
Reduction of halosilanes: 1.6.4.2.1
Reduction of halostannanes: 1.6.4.4.1
- C₄H₁₁As**
(C₂H₅)₂AsH
Formation: 1.5.3.3.3, 1.5.5.3.1
- C₄H₁₁BrSn**
(C₂H₅)₂SnH(Br)
Formation: 1.6.4.4.1
- C₄H₁₁ClGe**
(C₂H₅)₂GeHCl
Formation: 1.6.4.3.1
- C₄H₁₁ClO₂Si**
(C₂H₅O)₂SiHCl
Reduction by LiBH₄: 1.6.5.2.1
- C₄H₁₁ClSi**
(C₂H₅)₂SiClH
Formation: 1.6.4.3.1
- C₄H₁₁ClSn**
(C₂H₅)₂SnHCl
Formation: 1.6.3.4.3, 1.6.4.4.1
- C₄H₁₁Cl₃GeO**
(C₂H₅)₂O·GeHCl₃
Formation: 1.6.4.3.1
- C₄H₁₁Cl₃OGe**
(C₂H₅)₂O·GeCl₃H
Formation: 1.6.4.3.1
- C₄H₁₁FGe**
n-C₄H₉GeH₂F
Redistribution: 1.6.4.3.1
- C₄H₁₁FSn**
(C₂H₅)₂SnHF
Formation: 1.6.4.4.1
- C₄H₁₁N**
(C₂H₅)₂NH
Formation: 1.5.3.1.3, 5.4.1.3
i-C₄H₉NH₂
Reaction with (CH₃)₂AsN(CH₃)₂:
1.5.3.1.3

- $n\text{-C}_4\text{H}_9\text{NH}_2$
Industrial synthesis: 1.5.6.1
 $t\text{-C}_4\text{H}_9\text{NH}_2$
Formation: 1.5.5.1
- $\text{C}_4\text{H}_{11}\text{O}_2\text{P}$**
 $(\text{CH}_3)_2\text{P}(\text{O})\text{OC}_2\text{H}_5$
Reaction with LiAlD_4 : 1.5.7.1.2
- $\text{C}_4\text{H}_{11}\text{O}_2\text{PS}_2$**
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{SH}$
Reaction with $(\text{C}_2\text{H}_5)_3\text{SiCH}=\text{CH}_2$:
 1.6.4.1.4
- $\text{C}_4\text{H}_{11}\text{O}_3\text{P}$**
 $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{H}$
Formation: 1.5.3.2.2
- $\text{C}_4\text{H}_{11}\text{P}$**
 $(\text{C}_2\text{H}_5)_2\text{PH}$
Formation: 1.5.3.2.3, 1.5.5.2.3
 $t\text{-C}_4\text{H}_9\text{PH}_2$
Formation: 1.5.3.2.3
- $\text{C}_4\text{H}_{11}\text{PS}$**
 $(\text{C}_2\text{H}_5)_2\text{P}(\text{S})\text{H}$
Formation: 1.5.3.2.1, 1.5.3.2.3
- $\text{C}_4\text{H}_{11}\text{Sb}$**
 $n\text{-C}_4\text{H}_9\text{SbH}_2$
Formation: 1.5.5.4
 $(\text{C}_2\text{H}_5)_2\text{SbH}$
Formation: 1.5.5.4
- $\text{C}_4\text{H}_{12}\text{AlLi}$**
 $\text{LiAl}(\text{CH}_3)_4$
Formation: 1.8.3.1, 1.8.3.2
- $\text{C}_4\text{H}_{12}\text{AlLiO}_4$**
 $\text{LiAl}(\text{OCH}_3)_4$
Formation: 1.6.5.1.2
- $\text{C}_4\text{H}_{12}\text{AsN}$**
 $(\text{CH}_3)_2\text{AsN}(\text{CH}_3)_2$
Reaction with primary amines 1.5.3.1.3
 $n\text{-C}_4\text{H}_9\text{As}(\text{H})\text{NH}_2$
Formation: 1.5.3.3.2
- $\text{C}_4\text{H}_{12}\text{ClNSi}$**
 $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2\text{Cl}$
Reduction by LiBH_4 : 1.6.5.2.3
- $\text{C}_4\text{H}_{12}\text{ClN}_2\text{P}$**
 $[(\text{CH}_3)_2\text{N}]_2\text{PCl}$
Reaction with NH_3 : 1.5.3.2.3
- $\text{C}_4\text{H}_{12}\text{F}_2\text{Si}_2$**
 $(\text{C}_2\text{H}_5)_2\text{SiHSiF}_2\text{H}$
Formation: 1.6.4.2.1
- $\text{C}_4\text{H}_{12}\text{Ge}$**
 $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{GeH}$
Formation: 1.6.4.3.1
 $(\text{C}_2\text{H}_5)_2\text{GeH}_2$
Exchange with halogermanes: 1.6.4.3.1
Formation: 1.6.4.3.1, 1.6.5.3.1
Reduction of $\text{C}_2\text{H}_5\text{I}$: 1.6.4.1.1
- $\text{C}_4\text{H}_{12}\text{Ge}_2\text{S}_2$**
 $[(\text{CH}_3)_2\text{GeS}]_2$
Reduction by Zn in H_2O : 1.6.3.3.1
- $\text{C}_4\text{H}_{12}\text{K}_2\text{P}_4$**
 $\text{K}_2(\text{CH}_3\text{P})_4$
Protonolysis to CH_3PH_2 : 1.5.3.2.3
- $\text{C}_4\text{H}_{12}\text{Li}_2\text{P}_4$**
 $\text{Li}_2(\text{CH}_3\text{P})_4$
Protonolysis to CH_3PH_2 : 1.5.3.2.3
- $\text{C}_4\text{H}_{12}\text{Li}_2\text{Si}_2$**
 $\text{Li}_2[(\text{CH}_3)_2\text{Si}]_2$
Hydrolysis: 1.6.3.2.1
- $\text{C}_4\text{H}_{12}\text{NP}$**
 $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2$
Reaction with $(\text{CH}_3)_2\text{PH}$: 1.5.4.1.3
- $\text{C}_4\text{H}_{12}\text{OSi}$**
 $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)\text{H}$
Formation: 1.6.3.2.3
- $\text{C}_4\text{H}_{12}\text{O}_2\text{Si}$**
 $(\text{C}_2\text{H}_5\text{O})_2\text{SiH}_2$
Formation: 1.6.5.2.1
- $\text{C}_4\text{H}_{12}\text{O}_2\text{Sn}$**
 $(\text{CH}_3)_2\text{Sn}(\text{OCH}_3)_2$
Reduction with B_2H_6 : 1.6.4.4.2
- $\text{C}_4\text{H}_{12}\text{P}_2$**
 $(\text{CH}_3)_4\text{P}_2$
Protonation by HCl: 1.5.3.2.3
Reaction with $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$: 1.5.3.2.3
- $\text{C}_4\text{H}_{12}\text{P}_2\text{S}_2$**
 $(\text{CH}_3)_2\text{P}(\text{S})\text{P}(\text{S})(\text{CH}_3)_2$
Hydrolysis to $(\text{CH}_3)_2\text{P}(\text{S})\text{H}$: 1.5.3.2.1
Reaction with H_2O and $(t\text{-C}_4\text{H}_9)_3\text{P}$:
 1.5.3.2.3
- $\text{C}_4\text{H}_{12}\text{Pb}$**
 $(\text{C}_2\text{H}_5)_2\text{PbH}_2$
Formation: 1.6.5.5
- $\text{C}_4\text{H}_{12}\text{Si}$**
 $(\text{C}_2\text{H}_5)_2\text{SiH}_2$
Formation: 1.6.4.2.1, 1.6.4.2.2
Industrial synthesis: 1.6.6.2
Reaction with SiF_2 : 1.6.4.2.1
Reduction of GeCl_4 : 1.6.4.3.1
- $\text{C}_4\text{H}_{12}\text{Si}_2$**
 $\text{CH}_3\text{SiH}(\text{CH}_3)_2\text{Si}(\text{H})\text{CH}_3$
Formation: 1.6.4.2.1
- $\text{C}_4\text{H}_{12}\text{Sn}$**
 $(\text{CH}_3)_4\text{Sn}$
Reaction with P_4 : 1.5.4.2.2
- $\text{C}_4\text{H}_{12}\text{Sn}$**
 $(\text{C}_2\text{H}_5)_2\text{SnH}_2$
Formation: 1.6.3.4.1, 1.6.4.4.1, 1.6.4.4.2,
 1.6.4.4.3, 1.6.5.4.1
Redistribution with R_2SnX_2 : 1.6.4.4.1

C₄H₁₂Sn *cont.*

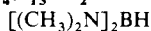
Formation: 1.6.5.4.1

C₄H₁₃AsGe

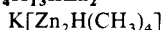
Redistribution: 1.5.4.3

C₄H₁₃AsSi

Redistribution: 1.5.4.3

C₄H₁₃BN₂

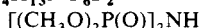
Formation: 1.7.3.3

C₄H₁₃KZn₂

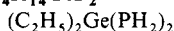
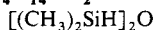
Formation: 1.9.4.2

From K[Zn(CH₃)₂H] with (CH₃)₂Zn:

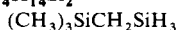
1.9.4.1

C₄H₁₃NO₆P₂

Formation: 1.5.3.1.3

C₄H₁₄GeP₂Redistribution to [(C₂H₅)₂Ge]₆P₄ andPH₃: 1.5.4.2.4**C₄H₁₄OSi₂**

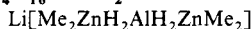
Formation: 1.6.3.2.1

Reaction with GeCl₄: 1.6.4.3.1**C₄H₁₄Si₂**

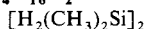
Formation: 1.6.4.2.3



Formation: 1.6.4.2.3

C₄H₁₆AlLiZn₂

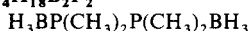
Formation: 1.9.5.2

C₄H₁₆Si₂

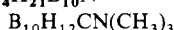
Formation: 1.6.3.2.1

C₄H₁₆Si₃

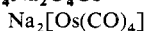
Formation: 1.6.2.2

C₄H₁₈B₂P₂

Pyrolysis: 1.5.4.2.4

C₄H₂₁B₁₀N

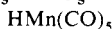
Reduction by Na: 1.6.4.1.3

C₄Na₂O₄Os

Protonation at metal: 1.10.6.2.1

C₅FeO₅Reaction with HSiPh₃: 1.10.5.4

Reaction with hydroxide: 1.10.9

C₅HMnO₅

Equilibrium acidity: 1.10.6.2.2

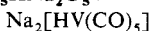
Formation: 1.10.3.2, 1.10.6.2.1, 1.10.9

Reaction with (C₆H₅)₃As: 1.6.4.1.5Reaction with CH₃AuP(C₆H₅)₃:

1.6.4.1.5

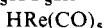
Reaction with C₆H₅C(CH₃)=CH₂:

1.6.4.1.4

C₅HNa₂O₅V

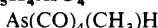
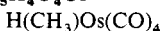
Formation by protonation of a metal

anion: 1.10.6.2.1

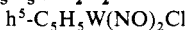
C₅HO₅Re

Equilibrium acidity: 1.10.6.2.2

Formation: 1.10.5.6.1, 1.10.6.2.1

C₅H₄AsO₄Reductive elimination of CH₄: 1.6.4.1.5**C₅H₄O₄Os**

Equilibrium acidity: 1.10.6.2.2

Reaction with H₂: 1.6.2.1.2**C₅H₅ClN₂O₂W**

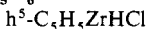
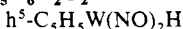
Reaction with alkoxyaluminum hydrides: 1.10.7.4

C₅H₅Li

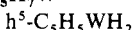
Reaction with HCl: 1.6.3.1.3

C₅H₅NProtonation in H₂O: 1.5.3.1.1Reduction by H₂ over Pt: 1.5.6.1**C₅H₆**

Formation: 1.6.2.5, 1.6.3.1.3, 1.6.4.3.3

Reaction with U[N(C₂H₅)₂]₄: 1.5.3.1.3**C₅H₆ClZr**Reaction with (C₆H₅)₂CN₂: 1.5.4.1.2**C₅H₆N₂O₂W**

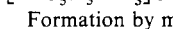
Formation: 1.10.7.4

C₅H₇WReaction with [C₆H₅N₂][PF₆]: 1.5.4.1.2Reaction with [p-CH₃C₆H₄N₂][PF₆]:

1.5.4.1.2

Reaction with [p-FC₆H₄N₂][PF₆]:

1.5.4.1.2

C₅H₈ClW

Formation by metal protonation:

1.10.6.1.1

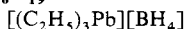
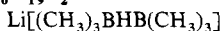
- C₅H₈Ge**
 C₅H₅GeH₃
 Disproportionation in presence of
 (C₂H₅)₂NH: 1.6.4.3.3
- C₅H₁₀**
 (CH₃)₂C(CH₂)₂
 Formation in carbon atom reaction
 with C₄H₁₀: 1.6.2.1.1
 n-C₅H₁₀
 Reaction with H₂ in presence of Pt:
 1.6.6.1
- C₅H₁₀BZr**
 h⁵-C₅H₅Zr(H)BH₄
 Reaction with Me₃N: 1.10.9
- C₅H₁₀ClOP**
 C₅H₁₀P(O)Cl
 Reduction by LiAlH₄: 1.5.5.2.1
- C₅H₁₀F₂OP**
 C₆H₄P(O-t-C₄H₉)F₂H
 Formation: 1.5.3.2.3
- C₅H₁₀N**
 Industrial synthesis: 1.5.6.1
- C₅H₁₀O**
 (C₂H₅)₂CO
 Reduction by NaBH₄: 1.6.5.1.2
- C₅H₁₁Br₃Ge**
 n-C₅H₁₁GeBr₃
 Reduction with LiAlH₄: 1.6.5.3.1
- C₅H₁₁Cl₃Si**
 C₅H₁₁SiCl₃
 Reduction by LiAlH₄: 1.6.6.2
- C₅H₁₁N**
 C₅H₁₀NH
 Formation: 1.5.3.1.3
- C₅H₁₁OP**
 t-C₄H₉C(O)PH₂
 Formation: 1.5.3.2.3
- C₅H₁₁O₂P**
 C₅H₁₀P(O)OH
 Reduction to C₅H₁₀P(O)OH: 1.5.4.2.2
- C₅H₁₁P**
 C₅H₁₀PH
 Formation: 1.5.4.2.2, 1.5.5.2.1
- C₅H₁₂**
 Industrial formation: 1.6.6.1
- C₅H₁₂O**
 (C₂H₅)₂CHOH
 Formation: 1.6.5.1.2
- C₅H₁₃B₂Zr**
 h⁵-C₅H₅Zr(BH₄)₂
 Reaction with Me₃N: 1.10.9
- C₅H₁₃Cl**
 (CH₃)₃CH(Cl)CH₃
 Industrial formation: 1.6.6.1
- C₅H₁₃O₃P**
 CH₃P(O)(OC₂H₅)₂
 Formation: 1.5.3.2.2
- C₅H₁₄Ge**
 n-C₅H₁₁GeH₃
 Formation: 1.6.5.3.1
- C₅H₁₄N₂**
 (CH₃)₂NCH₂CH₂NHCH₃
 Reacts with ZnH₂: 1.9.4.1
- C₅H₁₄Si**
 C₅H₁₁SiH₃
 Industrial formation: 1.6.6.2
- C₅H₁₅AsSi**
 (CH₃)₃SiAs(CH₃)₂
 Cleavage by H₂O: 1.5.3.3.3
 Reaction with (CF₃)₂PH: 1.5.4.2.3
- C₅H₁₅ClSi₂**
 (CH₃)₃SiSiCl(CH₃)₂
 Thermolysis: 1.6.4.2.1
- C₅H₁₅GeN**
 (CH₃)₃GeN(CH₃)₂
 Reaction with CH₃AsH₂: 1.5.4.1.3
- C₅H₁₅NsSn**
 (CH₃)₃SnNHC₂H₅
 Redistribution: 1.5.4.1.3
- C₅H₁₅N₂P**
 CH₃P[N(CH₃)₂]₂
 Reaction with HN[CH₂CH(CH₃)OH]₂:
 1.5.3.2.3
- C₅H₁₅PSi**
 (CH₃)₃SiP(CH₃)₂
 Reaction with (CF₃)₂PH: 1.5.4.2.3
- C₅H₁₆Ge₂**
 (CH₃)₃GeGeH(CH₃)₂
 Thermolysis: 1.6.4.3.3
- C₅H₁₆NPSSi**
 (CH₃)₂P(S)NHSi(CH₃)₃
 Formation: 1.5.3.1.3
- C₅H₁₆Si₂**
 (CH₃)₃SiCH₂SiH₂CH₃
 Formation: 1.6.4.2.3
- C₅H₁₈BPSi**
 (CH₃)₃SiP(CH₃)₂BH₃
 Disproportionation: 1.6.4.2.3
- C₅NaO₅Re**
 Na[Re(CO)₅]
 Protonation at metal: 1.10.6.2.1
- C₅Na₃O₅V**
 Na₃[V(CO)₅]
 Protonation at metal: 1.10.6.2.1
- C₅O₅Os**
 Os(CO)₅
 Reaction with H₂: 1.10.3.2

- C₆BF₄MnO₆**
 [Mn(CO)₆][BF₄]
 Reaction with H₂O: 1.10.9
- C₆CrO₆**
 Cr(CO)₆
 Reaction with [OH]⁻: 1.10.9
- C₆D₆**
 Formation: 1.6.7.2.1
- C₆F₃MnO₈**
 [Mn(CO)₅][O₃SCF₃]
 Formation by protonation of HMn(C*O)₅: 1.10.6.2.1
- C₆HF₅**
 C₆F₅H
 Formation: 1.6.3.1.3
- C₆HO₆V**
 HV(CO)₆
 Equilibrium acidity: 1.10.6.2.2
- C₆H₄BrO₅Re**
 Br(OC)₄ReC(OH)CH₃
 Formation by protonation of an acyl anion: 1.10.6.2.1
- C₆H₄F₇N₂P**
 [p-FC₆H₄N₂][PF₆]
 Reaction with h⁵-C₅H₅WH₂: 1.5.4.1.2
- C₆H₅BiBr₂**
 C₆H₅BiBr₂
 Reduction by Li[AlH₄]: 1.5.5.5
- C₆H₅Cl₂OP**
 C₆H₅P(O)Cl₂
 Reduction by Li[AlH₄]: 1.5.5.2.1
 Reaction with Li[AlD₄]: 1.5.7.1.2
 Reaction with HN[CH₂CH(CH₃)OH]₂: 1.5.3.2.3
- C₆H₅Cl₂P**
 C₆H₅PCL₂
 Hydrolysis to form C₆H₅PH(O)OH: 1.5.6.2
 Reaction with C₂H₅OH: 1.5.6.2
 Reaction with LiH: 1.5.4.2.1
 Reaction with HF: 1.5.3.2.3
 Reaction with diols: 1.5.3.2.3
 Reduction by (C₆H₅)₂SiH₂ or HSiCl₃: 1.5.4.2.2
- C₆H₅Cl₃Ge**
 C₆H₅GeCl₃
 Reduction by LiAlH₄: 1.6.6.3
- C₆H₅Cl₃Si**
 C₆H₅SiCl₃
 Reduction by Li[AlH₄]: 1.6.5.2.1, 1.6.6.2
 Reduction by LiH: 1.6.6.2
- C₆H₅Cl₃Sn**
 C₆H₅SnCl₃
 Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
 Reduction by Na[BH₄]: 1.6.5.4.2
- C₆H₅D**
 Formation: 1.6.7.1.1
- C₆H₅D₂N**
 C₆H₅ND₂
 Formation: 1.5.7.1.1
- C₆H₅D₂P**
 C₆H₅PD₂
 Formation: 1.5.7.1.2
- C₆H₅F₂P**
 C₆H₅PF₂
 Alcoholysis: 1.5.3.2.3
 Hydrolysis: 1.5.3.2.3
- C₆H₅F₆N₂P**
 C₆H₅N₂[PF₆]
 Reaction with h⁵-C₅H₅WH₂: 1.5.4.1.2
- C₆H₅I**
 C₆H₅I
 Reduction by NaH: 1.6.4.1.1
- C₆H₅I₂Sb**
 C₆H₅SbI₂
 Reduction by Li[BH₄]: 1.5.5.4
- C₆H₅NO**
 Reaction with H₂: 1.5.2.1.2
 Reaction with D₂ over Pt: 1.5.7.1.1
- C₆H₅NO₂**
 Industrial conversion to C₆H₅NH₂: 1.5.6.1
 Reaction with H₂: 1.5.2.1.2
 Reduction by Li[AlD₄]: 1.5.7.1.1
 Reduction by CaH₂: 1.5.4.1.1
 Reduction by carbon in steam: 1.5.6.1
 Reduction with D₂ over Pt: 1.5.7.1.1
- C₆H₅Na₃P**
 Na₂[C₆H₅P]
 Reaction with D₂O: 1.5.7.1.2
- C₆H₅O₅Rh**
 Rh(CO)₂CH₃COCH₂CO₂
 Catalyst in formation of (CH₂OH)₂: 1.6.2.1.2
- C₆H₆**
 C₆H₆
 Exchange with D₂, DF or DBr: 1.6.7.2.1
 Protonation in strong-acid media: 1.6.3.1.3
 Reaction with AsCl₃: 1.5.4.3, 1.5.6.3
 Reaction with H₂: 1.6.2.1.2
 CH₃C≡CC≡CCH₃
 Reaction with R₂SnH₂: 1.6.4.1.4
- C₆H₆B₂Fe₂O₆**
 Fe₂(B₂H₆)₂(CO)₆
 Thermolysis: 1.10.5.2
- C₆H₆FOP**
 C₆H₅P(O)FH
 Disproportionation to C₆H₅PF₂ and C₆H₅PF₃H: 1.5.3.2.3

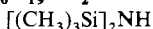
- Formation: 1.5.3.2.3
- C₆H₆F₂Ge**
C₆H₅GeF₂H
Formation: 1.6.4.3.1
- C₆H₆NO₂Re**
h⁵-C₅H₅Re(CO)(NO)H
Formation: 1.10.9
- C₆H₆O₂**
1,2-(HO)₂C₆H₄
Reaction with C₆H₄O₂P(Cl)NSO₂C₆*
H₄Cl: 1.5.3.1.3
- C₆H₇As**
C₆H₅AsH₂
Formation: 1.5.3.3.1, 1.5.4.3, 1.5.5.3.1, 1.5.6.3
- C₆H₇AsF₆**
(CH₃)₂AsC(CF₃)=C(CF₃)H
Formation: 1.6.4.1.4
- C₆H₇AsO₂**
C₆H₅As(OH)₂
Reduction by Zn amalgam in acid: 1.5.3.3.1
- C₆H₇N**
C₆H₅NH₂
Formation: 1.5.2.1.2, 1.5.3.1.2, 1.5.3.1.3, 1.5.4.1.1, 1.5.4.1.3
Industrial synthesis: 1.5.6.1
Protonation in H₂O: 1.5.3.1.1
Reaction with [(C₂H₅)₂N]₃P: 1.5.3.1.3
- C₆H₇O₂P**
C₆H₅PH(O)OH
Industrial synthesis: 1.5.6.2
Thermal disproportionation: 1.5.6.2
- C₆H₇O₃P**
C₆H₅P(O)(OH)₂
Reduction by LiAlH₄: 1.5.5.2.2
- C₆H₇P**
C₆H₅PH₂
Formation: 1.5.3.2.3, 1.5.5.2.1, 1.5.5.2.2
Reaction with (C₆H₅P)₃: 1.5.4.2.4
Synthesis from C₆H₅PH(O)₂OH: 1.5.6.2
- C₆H₇Sb**
C₆H₅SbH₂
Formation: 1.5.5.4
- C₆H₈Ge**
C₆H₅GeH₃
Disproportionation at 200°C: 1.6.4.3.3
Industrial synthesis: 1.6.6.3
- C₆H₈NP**
o-NH₂C₆H₄PH₂
Formation: 1.5.5.2.2
- C₆H₈Si**
C₆H₅SiH₃
Formation: 1.6.5.2.1
Industrial synthesis: 1.6.6.2
- C₆H₈Sn**
C₆H₅SnH₃
Formation: 1.6.4.4.3, 1.6.5.4.2
- C₆H₈B**
(CH₂=CH)₃B
Reaction with HCl: 1.6.3.1.3
- C₆H₉Cl₈NSb**
[NH₄][C₆H₅SbCl₅]
Reduction by LiAlH₄: 1.5.5.4
- C₆H₉F₆NSn**
(CH₃)₃SnNC(CF₃)₂
Reaction with PtHCl[P(C₆H₅)₃]₂: 1.5.4.1.2
- C₆H₉MoNO₄P**
h⁵-Mo(CO)₂P(OCH₂CH₂)₂NH
Formation: 1.5.3.1.3
- C₆H₉O₃P**
(CH₃CO)₃P
Reaction with CH₃OH: 1.5.3.2.3
- C₆H₁₀**
Formation: 1.6.4.1.2
Reaction with [(CH₃)₂Si]₆: 1.6.4.2.3
- C₆H₁₀N₂O₄**
(C₂H₅CO₂N)₂
Formation: 1.5.3.1.3
- C₆H₁₀Pb**
(C₂H₃)₃PbH
Formation: 1.6.4.5.3
- C₆H₁₁BrMg**
BrMgCH₂CH(C₂H₅)CH=CH₂
Thermal rearrangement: 1.6.4.1.5
- C₆H₁₁ClMg**
C₆H₁₁MgCl
Reaction with (C₆H₅)₃SiCl: 1.6.4.2.1
- C₆H₁₁NO₂**
Dehydrogenation-reduction: 1.5.2.1.2
- C₆H₁₂**
(CH₃)₃CCH=CH₂
Formation: 1.6.2.1.2
Reaction with HCl: 1.6.6.1
n-C₄H₉CHCH₂
Reaction with CO and H₂: 1.6.2.1.2
- C₆H₁₂NO₃P**
P(OCH₂CH₂)₃N
Protonation by [R₃O][BF₄]: 1.5.3.2.3
- C₆H₁₃BF₄NO₃P**
[HP(OCH₂CH₂)₃N]BF₄
Formation: 1.5.3.2.3
- C₆H₁₃ClMnO₆**
[Mo(CH₂CH₂NH)₃(NO)₂H][ClO₄]
Equilibrium acidity at metal: 1.10.6.1.2
- C₆H₁₃Cl₃Si**
C₆H₁₃SiCl₃
Reduction by Li[AlH₄]: 1.6.6.2

- C₆H₁₃P**
 C₆H₁₁PH₂
 Formation: 1.5.3.2.3
- C₆H₁₄Cl₂Pb**
 (i-C₃H₇)₂PbCl₂
 Reduction by Li[AlH₄]: 1.6.5.5
- C₆H₁₅Al**
 Al(C₂H₅)₃
 Catalyst in K[AlH₄] formation: 1.7.4.2
 Formation: 1.6.5.1.4
 Reduction with Na and H₂: 1.7.2
- C₆H₁₅As**
 (n-C₃H₇)₂AsH
 Formation: 1.5.5.3.1
- C₆H₁₅B**
 (C₂H₅)₃B
 Formation: 1.6.5.1.4
 Industrial formation: 1.6.6.1
- C₆H₁₅BDLi**
 Li[B(C₂H₅)₃D]
 Reduction of C₆H₅CHO: 1.6.7.1.1
- C₆H₁₅BrGe**
 (C₂H₅)₃GeBr
 Reduction by Zn in H₂O: 1.6.3.3.1
- C₆H₁₅ClGe**
 (C₂H₅)₃GeCl
 Reduction with LiAlH₄: 1.6.5.3.1
- C₆H₁₅ClGeMg**
 (C₂H₅)₃GeMgCl
 Hydrolysis: 1.6.3.3.1
- C₆H₁₅ClPb**
 (C₂H₅)₃PbCl
 Exchange reaction with (n-C₄H₉)₃SnH:
 1.6.4.5.1
 Reduction by LiAlH₄: 1.6.5.5
 Reduction with (C₂H₅)₂AlH: 1.6.4.5.1
- C₆H₁₅ClSi**
 (C₂H₅)₃SiCl
 Reduction with LiAlH₄: 1.6.5.2.1
- C₆H₁₅ClSn**
 (C₂H₅)₃SnCl
 Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
 Reduction with LiAlH₄: 1.6.6.4
- C₆H₁₅DSn**
 (C₂H₅)₃SnD
 Reduction of C₆H₅COCH₃: 1.6.7.1.1
- C₆H₁₅FSi**
 (C₂H₅)₃SiF
 Reduction by (C₂H₅)₂AlH: 1.6.4.2.1
 Reduction by Na-H₂: 1.6.4.2.1
- C₆H₁₅GeK**
 K[(C₂H₅)₃Ge]
 Hydrolysis: 1.6.3.3.1
- C₆H₁₅GeLi**
 Li[(C₂H₅)₃Ge]
 Hydrolysis: 1.6.3.3.1
 Reaction with GeH₄: 1.6.3.3.3
- C₆H₁₅GeNa**
 Na[(C₂H₅)₃Ge]
 Hydrolysis: 1.6.3.3.1
- C₆H₁₅LiPb**
 Li[(C₂H₅)₃Pb]
 Reaction with NH₄Br in liq NH₃:
 1.6.3.5
- C₆H₁₅N**
 (C₂H₅)₃N
 Complex formation with BH₃: 1.7.2
 Reaction with mineral acids to form ammonium salts: 1.5.6.1
 N(C₂H₅)₃
- C₆H₁₅NO₂**
 HN[CH₂CH(CH₃)OH]₂
 Reaction with CH₃P[N(CH₃)₂]₂:
 1.5.3.2.3
 Reaction with C₆H₅OPCl₂: 1.5.3.2.3
- C₆H₁₅NaSn**
 Na[(C₂H₅)₃Sn]
 Reaction with NH₄Br in liq NH₃:
 1.6.3.4.2
- C₆H₁₅O₂P**
 C₂H₅P(OC₂H₅)₂
 Reduction by LiAlH₄: 1.5.6.2
 t-C₄H₉P(O)(OC₂H₅)H
 Formation: 1.5.3.2.2
- C₆H₁₅O₃P**
 (C₂H₅O)₃P
 Protonation in strong acid: 1.5.3.2.3
 (i-C₃H₇O)₂P(O)H
 Formation: 1.5.3.2.3
 C₂H₅P(O)(OC₂H₅)₂
 Reduction by LiAlH₄: 1.5.5.2.2
- C₆H₁₅Sb**
 (C₂H₅)₃Sb
 Reaction with Ph₃SiH: 1.6.4.1.5
- C₆H₁₆AlNa**
 Na[Al(C₂H₅)₃H]
 Formation: 1.7.4.2
- C₆H₁₆BLi**
 Li[(C₂H₅)₃BH]
 Reduction of [Re(CO)₅P(C₆H₅)₃]⁺:
 1.6.5.1.2
 Reduction of C₆H₅CHO: 1.6.5.1.2
- C₆H₁₆CIN**
 [(C₂H₅)₃NH]Cl
 Industrial formation: 1.5.6.1

- C₆H₁₆F₂GeSn**
 (C₂H₅)₃SnGeF₂H
 Formation: 1.6.4.3.1
- C₆H₁₆F₂Ge₂**
 (C₂H₅)₃GeGeF₂H
 Formation: 1.6.4.3.1
- C₆H₁₆Ge**
 (C₂H₅)₃GeH
 Formation: 1.6.3.3.1, 1.6.3.3.2, 1.6.3.3.3,
 1.6.4.3.1, 1.6.4.3.3, 1.6.5.3.1
 Reaction with GeF₂: 1.6.4.3.1
 Reaction with GeCl₄: 1.6.4.3.1
 Reaction with [(C₂H₅)₃Si]₃Bi: 1.6.4.2.3
 (i-C₃H₇)₂GeH₂
 Formation: 1.6.4.3.1
- C₆H₁₆NP**
 (C₂H₅)₂PN(CH₃)₂
 Reaction with H₂S: 1.5.3.2.3
- C₆H₁₆N₂**
 (CH₃)₂C(NH₂)CNH₂(CH₃)₂
 Formation: 1.5.5.1
- C₆H₁₆OSi**
 (CH₃)₂Si(OC₄H₉-n)H
 Formation: 1.6.3.2.3
- C₆H₁₆O₂Si**
 (CH₃)₂Si(OC₂H₅)₂
 Reaction with LiAlH₄: 1.6.5.2.2
 Reaction with (C₂H₅)₂AlH: 1.6.4.2.2
 C₂H₅SiH(OC₂H₅)₂
 Redistribution: 1.6.4.2.2
- C₆H₁₆O₂Sn**
 (C₂H₅)₂Sn(OCH₃)₂
 Reaction with B₂H₆: 1.6.4.4.2
- C₆H₁₆Pb**
 (C₂H₅)₃PbH
 Formation: 1.6.3.5, 1.6.4.5.1, 1.6.4.5.2,
 1.6.4.5.3, 1.6.5.5
 (i-C₃H₇)₂PbH₂
 Formation: 1.6.5.5
- C₆H₁₆Si**
 (CH₃)₃SiCH₂CH₂CH₃
 Formation: 1.6.6.1
 (C₂H₅)₃SiH
 Formation: 1.6.2.2, 1.6.4.2.1, 1.6.4.2.3,
 1.6.5.2.1
 Reaction with GeF₂: 1.6.4.3.1
 Reaction with (C₂H₅)₃SiH: 1.6.4.2.3
 Reaction with C₂H₅NCS: 1.6.4.1.3
 Reduction of C₆H₅CH₂OH: 1.6.4.1.2
- C₆H₁₆Sn**
 (C₂H₅)₃SnH
 Formation: 1.6.2.4, 1.6.3.4.1, 1.6.3.4.2,
 1.6.4.4.3, 1.6.5.4.3
- Industrial formation: 1.6.6.4
 Reaction with GeF₂: 1.6.4.3.1
 Reaction with [(C₂H₅)₃Ge]₂Cd:
 1.6.4.3.3
 Reaction with [(C₂H₅)₃Ge]₃Tl: 1.6.4.3.3
 Reaction with C₆H₁₁NCNC₆H₁₁:
 1.6.4.1.3
 Reaction with C₆H₅COCH₃: 1.6.4.1.2
 Reaction with C₆H₅CH=CH₂: 1.6.4.1.4
 (n-C₃H₇)₂SnH₂
 Formation: 1.6.4.4.2
- C₆H₁₆Si**
 C₆H₁₃SiH₃
 Industrial formation: 1.6.6.2
- C₆H₁₇NSi**
 (CH₃)₂SiN(C₂H₅)₂H
 Formation: 1.6.3.2.3
- C₆H₁₈Al₂**
 Al₂(CH₃)₆
 Reaction with B₂H₆: 1.7.3.2
- C₆H₁₈F₂NPSi₂**
 [(CH₃)₃Si]₂NPF₂
 Reduction by LiAlH₄: 1.5.5.2.1
- C₆H₁₈GeSi**
 (CH₃)₃SiGe(CH₃)₃
 Formation: 1.6.4.3.3
- C₆H₁₈Ge₂**
 (CH₃)₃GeGe(CH₃)₃
 Formation: 1.6.4.3.3
- C₆H₁₈HgSn₂**
 [(CH₃)₃Sn]₂Hg
 Exchange reaction with (C₆H₅)₃SnH:
 1.6.4.4.3
- C₆H₁₈Li₂Si₃**
 Li₂[(CH₃)₂Si]₃
 Hydrolysis: 1.6.3.2.1
- C₆H₁₈NNaSi₂**
 Na[[[(CH₃)₃Si]₂N]
 Reaction with D₂O: 1.5.3.1.3
- C₆H₁₈N₃P**
 [(CH₃)₂N]₃P
 Reactions with cyclic tetramines:
 1.5.3.2.3
 Reaction with C₂H₅OH: 1.5.3.1.2
 Reaction with H₂S: 1.5.3.2.3
- C₆H₁₈OSi₂**
 (CH₃)₃SiOSi(CH₃)₃
 Photolytic decomposition: 1.6.4.1.5
 Reduction by (C₄H₉)₂AlH: 1.6.4.2.2
- C₆H₁₉AsSi₂**
 [(CH₃)₃Si]₂AsH
 Formation: 1.5.4.3

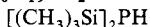
C₆H₁₉BPbReaction with CH₃OH: 1.6.4.5.2**C₆H₁₉B₂Li**

Formation: 1.7.5.1

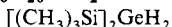
C₆H₁₉NSi₂

Formation: 1.5.3.1.3

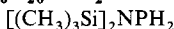
Reaction with DCl: 1.5.7.1.1

C₆H₁₉PSi₂

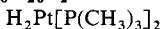
Formation: 1.5.4.2.4

C₆H₂₀GeSi₂

Formation: 1.6.2.3

C₆H₂₀NPSi₂

Formation: 1.5.5.2.1

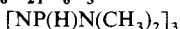
C₆H₂₀P₂Pt

Formation: 1.10.4.3.4

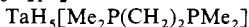
C₆H₂₀Si₃

Formation: 1.6.3.2.1

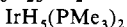
Thermolysis: 1.6.4.2.3

C₆H₂₁N₆P₃

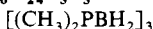
Formation: 1.5.3.2.3

C₆H₂₁P₂Ta

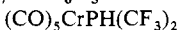
Formation: 1.10.3.2

C₆H₂₃IrP₂

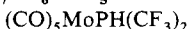
Formation: 1.10.7.2

C₆H₂₄B₃P₃

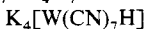
Formation: 1.6.4.2.3

C₆O₆WReaction with NaBH₄: 1.10.9**C₇HCrF₆O₅P**

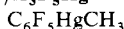
Formation: 1.5.3.2.3

C₇HF₆MoO₅P

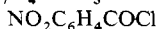
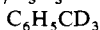
Formation: 1.5.3.2.3

C₇HK₄N₇W

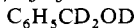
Formation by protonation of a metal anion: 1.10.6.2.1

C₇H₃F₅Hg

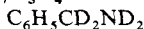
Reaction with HCl: 1.6.3.1.3

C₇H₄ClNO₃Reduction with LiHAL(OC₄H₉-t)₃: 1.6.5.1.1**C₇H₅D₃**

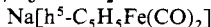
Formation: 1.6.7.2.1

C₇H₅D₃O

Formation: 1.6.7.1.1

C₇H₅D₄N

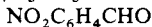
Formation: 1.5.7.1.1, 1.6.7.1.1

C₇H₅F₆NO₃PreReaction with [OH]⁻: 1.10.9**C₇H₅FeNaO₂**

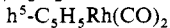
Protonation at metal: 1.10.6.2.1

C₇H₅N

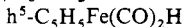
Reaction with HCl or HBr: 1.5.6.1

Reaction with H₂: 1.6.2.1.2Reduction by BH₃ in THF: 1.6.4.1.3Reduction by D₂ over Pt: 1.5.7.1.1**C₇H₅NO**Reaction with (C₆H₅)₃SnH: 1.6.4.1.3**C₇H₅NO₃**

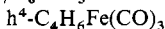
Formation: 1.6.5.1.1

C₇H₅O₂RhReaction with HSiPh₃: 1.10.5.4**C₇H₆D₂O**

Formation: 1.6.7.1.1

C₇H₆FeO₂

Formation by protonation of a metal anion: 1.10.6.2.1

Reaction with C₂F₄: 1.6.4.1.4**C₇H₆FeO₃**

Reaction with HCl: 1.6.3.1.3

C₇H₆NO₃ReReaction with BH₃ or (t-C₄H₉)₂AlH: 1.6.4.1.2

C₇H₆NO₄Re

h⁵-C₅H₅Re(CO)(NO)CO₂H
Formation of hydride: 1.10.9

C₇H₆O

C₆H₅CHO
Reduction by Li[(C₂H₅)₃BH]: 1.6.5.1.2
Reduction with Li[B(C₂H₅)₃D]:
1.6.7.1.1

C₇H₆O₂

C₆H₅CO₂H
Reaction with LiAlH₄: 1.6.5.1.2
Reaction with LiAlD₄: 1.6.7.1.1

C₇H₆O₂Ru

h⁵-C₅H₅Ru(CO)₂H
Equilibrium acidity: 1.10.6.2.2

C₇H₇AsCrO₅

(CO)₅Cr(CH₃)₂AsH
Formation: 1.5.4.3

C₇H₇AsMoO₅

(CO)₅Mo(CH₃)₂AsH
Formation: 1.5.4.3

C₇H₇Br

C₆H₅CH₂Br
Reaction with B₂H₆: 1.6.4.1.1

C₇H₇Cl

C₆H₅CH₂Cl
Reduction by alkali-metal hydrides:
1.6.4.1.1
Reduction with LiD: 1.6.7.1.1

C₇H₇ClFeO₃

h³-CH₃C₃H₄FeCl(CO)₃
Formation: 1.6.3.1.3

C₇H₇Cl₂N

[C₆H₅CClNH₂]₂Cl
Formation from reaction of C₆H₅CN
with HCl: 1.5.6.1

C₇H₇Cl₂P

C₆H₅CH₂PCl₂
Hydrolysis to form C₆H₅CH₂PH(O)O*
H: 1.5.6.2

C₇H₇CoN₂O₂

h⁵-C₅H₅Co(NO)₂C₂H₂
Reduction by LiAlH₄: 1.5.5.1

C₇H₇CrPO₅

(CO)₅CrPH(CH₃)₂
Formation: 1.5.3.2.3

C₇H₇D

C₆H₅CH₂D
Formation: 1.6.7.1.1

C₇H₇F₆N₂P

p-CH₃C₆H₄N₂[PF₆]
Reaction with h⁵-C₅H₅WH₂: 1.5.4.1.2

C₇H₇MoPO₅

(CO)₅MoPH(CH₃)₂
Formation: 1.5.3.2.3

C₇H₇NO

C₆H₅CONH₂
Reduction by Zn: 1.6.3.1.3
C₆H₅NHCOH
Formation: 1.5.4.1.3

C₇H₇O₂Re

h⁵-C₅H₅ReH₂(CO)₂
Formation: 1.10.4.3.2

C₇H₈

C₆H₅CH₃
Exchange with ND₃: 1.6.7.2.1
Formation: 1.6.2.1.1, 1.6.2.1.2, 1.6.3.1.2,
1.6.4.1.1, 1.6.4.1.2
Reaction with H₂ over Pt-SiO₂: 1.6.6.1

C₇H₈BCl₂N

C₆H₅(CH₃)NBCl₂
Hydrolysis to C₆H₅(CH₃)NH: 1.5.3.1.1

C₇H₈NO₂Re

h⁵-C₅H₅Re(CO)(NO)CH₃
Formation: 1.6.4.1.2, 1.6.5.1.2

C₇H₈NO₃Re

h⁵-C₅H₅Re(NO)(CO)CH₂OH
Formation: 1.6.4.1.2

C₇H₈O

C₆H₅CH₂OH
Formation: 1.6.5.1.2
Reduction by Et₃SiH in CF₃CO₂H:
1.6.4.1.2

C₇H₉As

C₆H₅(CH₃)AsH
Formation: 1.5.3.3.1

C₇H₉AsO

p-CH₃OC₆H₄AsH₂
Formation: 1.5.3.3.1

C₇H₉AsO₂

C₆H₅(CH₃)AsO₂H
Reduction by Zn amalgam in acid:
1.5.3.3.1

C₇H₉AsO₄

p-CH₃OC₆H₄AsO(OH)₂
Reduction by Zn in acid: 1.5.3.3.1

C₇H₉F₂OP

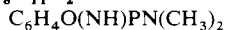
C₆H₅P(OCH₃)₂H
Formation: 1.5.3.2.3

C₇H₉N

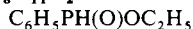
C₆H₅CH₂NH₂
Formation: 1.6.2.1.2, 1.6.3.1.3

- C₇H₉OP**
 $\text{C}_6\text{H}_5(\text{CH}_3)\text{P}(\text{O})\text{H}$
 Formation: 1.5.5.2.3
- C₇H₉O₂P**
 $\text{C}_6\text{H}_5\text{CH}_2\text{PH}(\text{O})\text{OH}$
 Industrial formation: 1.5.6.2
- C₇H₉P**
 $\text{C}_6\text{H}_5\text{CH}_2\text{PH}_2$
 Formation: 1.5.5.2.2
 $\text{C}_6\text{H}_5(\text{CH}_3)\text{PH}$
 Formation: 1.5.5.2.2
- C₇H₁₀P₂**
 $\text{C}_6\text{H}_5\text{P}(\text{H})\text{CH}_2\text{PH}_2$
 Formation: 1.5.5.2.2
- C₇H₁₄**
 $\text{CH}_3\text{C}_6\text{H}_{11}$
 Formation: 1.6.2.1.2
 Industrial formation: 1.6.6.1
- C₇H₁₆Ge**
 $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{CH}_2)_3$
 Reaction with germane: 1.6.4.3.3
 Reaction with silanes: 1.6.4.3.3
- C₇H₁₆O**
 $n\text{-C}_7\text{H}_{15}\text{OH}$
 Formation: 1.6.2.1.2
- C₇H₁₆O₃**
 $(\text{C}_2\text{H}_5\text{O})_3\text{CH}$
 Reaction with $\text{Al}(\text{BH}_4)_3$: 1.6.5.1.2
- C₇H₁₆Si**
 $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{CHCH}_2$
 Formation: 1.6.4.1.4
- C₇H₁₇Al**
 $(\text{C}_2\text{H}_5)_2\text{Al}(\text{CH}_2)_2\text{CH}_3$
 Formation: 1.6.6.1
- C₇H₁₇O₃P**
 $\text{CH}_3\text{P}(\text{O})(\text{OC}_3\text{H}_7\text{-i})_2$
 Formation: 1.5.3.2.2
- C₇H₁₈ClIrOP₂**
 $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$
 Reaction with B_5H_9 : 1.10.5.2
- C₇H₁₈Pb**
 $(\text{CH}_3)_3\text{Pb}(\text{CH}_2)_2\text{C}_2\text{H}_5$
 Formation: 1.6.4.1.4
- C₇H₁₉NPb**
 $(\text{CH}_3)_3\text{PbN}(\text{C}_2\text{H}_5)_2$
 Reaction with $(\text{CH}_3)_3\text{SnH}$: 1.5.4.1.3
- C₇H₁₉NSi**
 $[(\text{CH}_3)_3\text{Si}](\text{CH}_3)_3\text{CNH}$
 Formation: 1.5.3.1.3
- C₇H₁₉NSn**
 $(\text{CH}_3)_3\text{SnN}(\text{C}_2\text{H}_5)_2$
 Reduction by B_2H_6 or $(\text{C}_4\text{H}_9)_2\text{AlH}$: 1.6.4.4.3
- C₇H₂₂Ge₃**
 $(\text{CH}_3)_3\text{GeGe}(\text{CH}_3)_2\text{Ge}(\text{CH}_3)_2\text{H}$
 Formation: 1.6.4.3.3
- C₇H₃₁B₁₀NSi₂**
 $\text{B}_{10}\text{H}_{13}\text{CN}[\text{Si}(\text{CH}_3)_3]_2$
 Reaction with H_2O : 1.5.3.1.3
- C₇K₅N₇W**
 $\text{K}_5[\text{W}(\text{CN})_7]$
 Protonation at metal: 1.10.6.2.1
- C₈Fe₂Na₂O₈**
 $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$
 Protonation of metal-metal bond: 1.10.6.2.4
- C₈H₂O₈Os₂**
 $\text{H}_2\text{Os}_2(\text{CO})_8$
 Equilibrium acidity and rate of formation by protonation of an anion: 1.10.6.2.4
- C₈H₅Cl**
 $\text{C}_6\text{H}_5\text{CCCl}$
 Reduction of LiAlH_4 : 1.6.5.1.4
- C₈H₅ClMoO₃**
 $\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$
 Reaction with $\text{C}_6\text{H}_5\text{P}(\text{H})(\text{OCH}_2\text{CH}_2)_2^*$: 1.5.3.1.3
- C₈H₅F₆MoO₃P**
 $[\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3][\text{PF}_6]$
 Reaction with $\text{Na}[\text{BH}_3\text{CN}]$: 1.10.7.2
- C₈H₅MoNaO₃**
 $\text{Na}[\text{h}^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]$
 Protonation at metal: 1.10.6.2.1
- C₈H₅Na₂NbO₃**
 $\text{Na}_2[\text{h}^5\text{-C}_5\text{H}_5\text{Nb}(\text{CO})_3]$
 Protonation at metal: 1.10.6.2.1
- C₈H₅O₃Re**
 $\text{h}^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3$
 Reaction with HSiPh_3 : 1.10.5.4
 Reaction with H_2 : 1.10.4.3.2
- C₈H₆**
 $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$
 Reaction with DBr: 1.6.7.1.1
 Reaction with $(n\text{-C}_4\text{H}_9)_3\text{GeH}$: 1.6.4.1.4
- C₈H₆Br₂D₂**
 $\text{C}_6\text{H}_5\text{CBr}_2\text{CHD}_2$
 Formation: 1.6.7.1.1

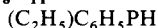
- C₈H₆CrO₃**
 $h^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{H}$
 Equilibrium acidity: 1.10.6.2.2
 Formation: 1.10.3.2
 Rate of formation by protonation of anion: 1.10.6.2.3
- C₈H₆FeO₄**
 $h^2\text{-C}_4\text{H}_6\text{Fe}(\text{CO})_4$
 Reaction with HCl: 1.6.3.1.3
- C₈H₆MoO₃**
 $h^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$
 Equilibrium acidity: 1.10.6.2.2
 Formation: 1.10.6.2.1, 1.10.7.2
 Rate of formation by protonation of anion: 1.10.6.2.3
 Reaction with $\{[(\text{CH}_3)_3\text{Si}]_2\text{CH}\}_2\text{Sn}$: 1.6.4.4.3
- C₈H₆NaNbO₃**
 $\text{Na}[h^5\text{-C}_5\text{H}_5\text{Nb}(\text{CO})_3\text{H}]$
 Generation by protonation of a metal anion: 1.10.6.2.1
- C₈H₆O₃W**
 $h^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$
 Equilibrium acidity: 1.10.6.2.2
 Protonation at metal: 1.10.6.1.1
 Rate of formation by protonation of anion: 1.10.6.2.3
- C₈H₇Cl**
 $\text{C}_6\text{H}_5\text{CH}=\text{CHCl}$
 Formation: 1.6.5.1.4
- C₈H₇ClFeO₄**
 $[h^2\text{-C}_4\text{H}_7\text{Fe}(\text{CO})_4]\text{Cl}$
 Formation: 1.6.3.1.3
- C₈H₈**
 $\text{C}_6\text{H}_5\text{CHCH}_2$
 Reaction with P₄ and O₂ to form C₆*
 $\text{H}_5\text{C}_6\text{H}(\text{OH})\text{CH}_2\text{PH}(\text{O})\text{OH}$: 1.5.6.2
 Reaction with (C₂H₅)₃SnH: 1.6.4.1.4
 Reaction with Li in liq NH₃: 1.6.3.1.2
 $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
 Reaction with (C₄H₉)₂AlH: 1.6.4.1.4
- C₈H₈D₂O**
 $\text{C}_6\text{H}_5(\text{CH}_3)\text{CDOD}$
 Formation: 1.6.7.1.1
- C₈H₈F₅OP**
 $\text{C}_6\text{H}_5\text{P}(\text{OCH}_2\text{CF}_3)_2\text{H}$
 Formation: 1.5.3.2.3
- C₈H₈FeO₃**
 $h^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{OH}$
 Formation: 1.6.5.1.2
- C₈H₈HgO₂**
 $\text{C}_6\text{H}_5\text{HgOCOCH}_3$
 Reaction with H₂ over Rh: 1.6.2.1.2
- C₈H₈O**
 $\text{C}_6\text{H}_5\text{COCH}_3$
 Reaction with (C₂H₅)₃SnH: 1.6.4.1.2
 Reduction by (C₆H₅)₂SiH₂: 1.6.4.1.2
 Reduction by (C₂H₅)₃SnD: 1.6.7.1.1
- C₈H₉AlCILI**
 $[\text{C}_6\text{H}_5\text{CHC}(\text{Cl})\text{AlH}_3]\text{Li}$
 Formation: 1.6.5.1.4
 Reaction with CH₃OH: 1.6.5.1.4
- C₈H₉N**
 $\text{C}_6\text{H}_5\text{CHNCH}_3$
 Reaction with H₂Os₃(CO)₁₀: 1.5.4.1.2
- C₈H₉NO**
 $\text{CH}_3(\text{C}_6\text{H}_5)\text{CNOH}$
 Reaction with H₂: 1.5.2.1.2
- C₈H₉P**
 $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{PH}$
 Formation: 1.5.4.2.2
 $\text{C}_6\text{H}_5\text{CH}=\text{CHPH}_2$
 Formation: 1.5.5.2.2
- C₈H₁₀**
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$
 Formation: 1.6.3.1.2
- C₈H₁₀NOP**
 $\text{C}_6\text{H}_4\text{O}(\text{NH})\text{PC}_2\text{H}_5$
 Reaction with C₆H₅SH: 1.5.3.2.3
 Reaction with C₂H₅OH: 1.5.3.2.3
 Reaction with C₆H₅OH: 1.5.3.2.3
 Reaction with CH₂CHOCOH: 1.5.3.2.3
- C₈H₁₀NO₃P**
 $\text{C}_6\text{H}_4\text{O}(\text{NH})\text{P}(\text{H})\text{O}_2\text{C}_2\text{H}_4$
 Formation: 1.5.3.2.3
- C₈H₁₀O**
 $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHOH}$
 Formation: 1.6.4.1.2
- C₈H₁₀Zr**
 $(\text{C}_8\text{H}_8)\text{ZrH}_2$
 Formation: 1.10.8.2
- C₈H₁₁As**
 $\text{C}_2\text{H}_5(\text{C}_6\text{H}_5)\text{AsH}$
 Formation: 1.5.3.3.3
- C₈H₁₁F₂OP**
 $\text{C}_6\text{H}_5\text{P}(\text{OC}_2\text{H}_5)_2\text{H}$
 Formation: 1.5.3.2.3
- C₈H₁₁N**
 $\text{CH}_3(\text{C}_6\text{H}_5)\text{CHNH}_2$
 Formation: 1.5.2.1.2

C₈H₁₁N₂OP

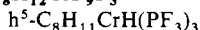
Reaction with diols: 1.5.3.2.3

C₈H₁₁O₂PSynthesis from $\text{C}_6\text{H}_5\text{PCl}_2$ and $\text{C}_2\text{H}_5\text{OH}$: 1.5.6.2**C₈H₁₁O₃P**

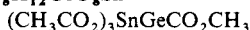
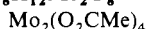
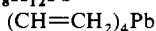
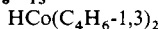
Industrial synthesis: 1.5.6.2

C₈H₁₁P

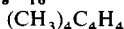
Formation: 1.5.3.2.3

C₈H₁₂CrF₉P₃

Formation: 1.10.2

C₈H₁₂GeO₈SnReduction by LiAlH_4 : 1.6.5.4.2**C₈H₁₂Mo₂O₈**Reaction with HCl : 1.10.5.1Reaction with H_2 and PMe_3 : 1.10.3.2**C₈H₁₂Pb**Reaction with B_2H_6 : 1.6.4.5.3**C₈H₁₃Co**

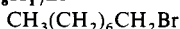
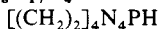
Formation: 1.10.2

C₈H₁₆

Formation: 1.6.2.5

C₈H₁₆Si

Formation: 1.6.4.2.3

C₈H₁₇BrReduction by $(\text{KC}_6\text{H}_5)_n$: 1.6.5.1.1**C₈H₁₇N₄P**

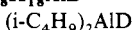
Formation: 1.5.3.2.3

C₈H₁₈

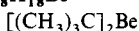
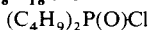
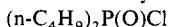
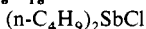
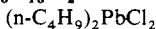
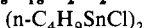
Formation: 1.6.5.1.1



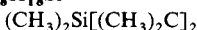
Formation: 1.6.6.1

C₈H₁₈AlD

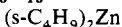
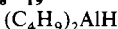
Formation: 1.7.4.2

C₈H₁₈BePyrolysis to form BeH_2 : 1.8.3.1**C₈H₁₈ClOP**Reduction by HSiCl_3 : 1.5.6.2Reduction by HSiCl_3 : 1.5.4.2.2**C₈H₁₈ClSb**Reduction by LiAlH_4 : 1.5.5.4**C₈H₁₈Cl₂Pb**Reduction by LiAlH_4 : 1.6.5.5**C₈H₁₈Cl₂Sn₂**Reduction by LiAlH_4 : 1.6.5.4.1**C₈H₁₈KP₃**Protonolysis to $(\text{t-C}_4\text{H}_9\text{P})_2\text{PH}$: 1.5.3.2.3**C₈H₁₈K₂P₂**Protonolysis to $(\text{t-C}_4\text{H}_9\text{P})_2\text{H}_2$: 1.5.3.2.3**C₈H₁₈OSn**Reaction with $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{Cl})\text{H}$:

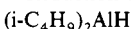
1.6.4.4.2

C₈H₁₈SiReaction with $(\text{C}_2\text{H}_5)_3\text{SiH}$: 1.6.4.2.3Reaction with $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{SH}$:

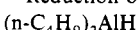
1.6.4.1.4

C₈H₁₈SnReaction with $(\text{CH}_3)_2\text{SnH}_2$: 1.6.4.4.3**C₈H₁₈Zn**Reduction to K_2ZnH_4 by KH : 1.9.4.1**C₈H₁₉Al**Reaction with $[(\text{CH}_3)_3\text{Si}]_2\text{O}$: 1.6.4.2.2

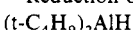
Reduction of aminostannanes: 1.6.4.4.3



Formation: 1.7.3.3, 1.7.4.2

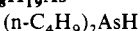
Reaction with GeO_2 : 1.6.4.3.2Reduction of $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$: 1.6.4.1.4

Reduction of aminostannanes: 1.6.4.4.3



Reduction of acyl metal complexes:

1.6.4.1.2

C₈H₁₉As

Formation: 1.5.5.3.1

- C₈H₁₉ClSn**
 (n-C₄H₉)₂SnClH
 Formation: 1.6.4.4.1
 Reaction with (n-C₄H₉)₂SnO: 1.6.4.4.2
- C₈H₁₉FSn**
 (n-C₄H₉)₂SnHF
 Formation: 1.6.4.4.1
- C₈H₁₉O₂P**
 (C₄H₉)₂P(O)OH
 Reduction by (C₆H₅)₂SiH₂: 1.5.6.2
- C₈H₁₉O₃P**
 (n-C₄H₉O)₂P(O)H
 Formation: 1.5.3.2.2
 n-C₄H₉P(O)(OC₂H₅)₂
 Reduction by silanes: 1.5.4.2.2
- C₈H₁₉P**
 (C₄H₉)₂PH
 Formation: 1.5.6.2
 (n-C₄H₉)₂PH
 Formation: 1.5.5.2.3
- C₈H₁₉PS**
 (n-C₄H₉)₂P(S)H
 Formation: 1.5.3.2.1
- C₈H₁₉P₂Rh**
 HRh[P(C₄H₉-t)]₂
 Reaction with H₂: 1.10.4.1.3
- C₈H₁₉P₃**
 (t-C₄H₉P)₂PH
 Disproportionation: 1.5.4.2.4
 Formation: 1.5.3.2.3
- C₈H₁₉Sb**
 (n-C₄H₉)₂SbH
 Formation: 1.5.4.4, 1.5.5.4
- C₈H₂₀K₂P₄**
 K₂[(C₂H₅P)₄]
 Protonolysis to C₂H₅PH₂: 1.5.3.2.3
- C₈H₂₀Li₂P₄**
 Li₂(C₂H₅P)₄
 Protonolysis to C₂H₅PH₂: 1.5.3.2.3
- C₈H₂₀NP**
 (C₂H₅)₂PN(C₂H₅)₂
 Reaction with H₂S: 1.5.3.2.3
- C₈H₂₀O₂Si**
 (C₂H₅)₂Si(OC₂H₅)₂
 Reduction by LiH: 1.6.4.2.2
- C₈H₂₀O₂Sn**
 (n-C₃H₇)₂Sn(OCH₃)₂
 Reduction by B₂H₆: 1.6.4.4.2
- C₈H₂₀O₄Si**
 (C₂H₅O)₄Si
 Reduction by NaAlBH₄: 1.6.5.2.2
 Reduction by Al(BH₄)₃: 1.6.5.2.2
- Reduction by LiAlH₄: 1.6.5.2.2
 Reduction by AlCl₃-NaCl-H₂ in Al*
 Cl₃-NaCl: 1.6.4.2.2
- C₈H₂₀O₄Sn**
 (C₂H₅O)₄Sn
 Reduction by (C₂H₅)₂AlH: 1.6.4.4.2
- C₈H₂₀P₂S₂**
 (C₂H₅)₂P(S)P(S)(C₂H₅)₂
 Hydrolysis to (C₂H₅)P(S)H: 1.5.3.2.1
- C₈H₂₀Pb**
 (n-C₄H₉)₂PbH₂
 Formation: 1.6.5.5
- C₈H₂₀Sn**
 (n-C₄H₉)₂SnH₂
 Exchange reactions with dihalostannanes: 1.6.4.4.1
 Formation: 1.6.4.4.2
 Reaction with CH₃C≡CC≡CCH₃: 1.6.4.1.4
- C₈H₂₁NO₆P₂**
 [(C₂H₅O)₂P(O)]₂NH
 Formation: 1.5.3.1.3
- C₈H₂₁NSn**
 (C₂H₅)₃SnNHC₂H₅
 Redistribution: 1.5.4.1.3
- C₈H₂₂P₂Pt**
 h²-C₂H₄Pt[P(CH₃)₃]₂
 Reaction with H₂: 1.10.4.3.4
- C₈H₂₂Si₂**
 (C₂H₅)₃SiSi(CH₃)₂H
 Formation: 1.6.4.2.3
- C₈H₂₄Li₂Si₄**
 Li₂[(CH₃)₂Si]₄
 Hydrolysis: 1.6.3.2.1
- C₈H₂₄MoN₄**
 Mo[N(CH₃)₂]₄
 Reaction with i-C₃H₇OH: 1.5.3.1.3
- C₈H₂₄NPSSi₂**
 (CH₃)₂P(S)N[Si(CH₃)₃]₂
 Reaction with H₂O: 1.5.3.1.3
- C₈H₂₆Si₄**
 H₂[(CH₃)₂Si]₄
 Formation: 1.6.3.2.1
- C₈H₃₄B₁₂O₂Zn**
 (THF)₂Zn(B₆H₉)₂
 Formation: 1.9.5.2
- C₈O₈Co₂**
 Co₂(CO)₈
 Reaction with H₂: 1.10.3.2
- C₉CrD₆O₃**
 h⁶-C₆D₆Cr(CO)₃
 Formation: 1.6.7.2.1

- C₉H₂O₉Os₃S**
 Os₃H₂(S)(CO)₉
 Formation: 1.10.5.6.2
- C₉H₃Cl₉O₉Os₃Si₃**
 Os₃(μ-H)₃(SiCl₃)₃(CO)₉
 Reaction with HSiCl₃: 1.10.5.4
- C₉H₅NbO₄**
 h⁵-C₅H₅Nb(CO)₄
 Protonation at metal: 1.10.6.1.1
- C₉H₅O₄V**
 h⁵-C₅H₅V(CO)₄
 Reaction with borohydride: 1.10.6.3
- C₉H₆AsCrF₆PO₅**
 (CF₃)₂PAs(CH₃)₂Cr(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.4.3
- C₉H₆AsF₆MoO₅PO₅**
 (CF₃)₂PAs(CH₃)₂Mo(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.4.3
- C₉H₆As₂CrF₆O₅**
 (CH₃)₂AsAs(CF₃)₂Cr(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.4.3
- C₉H₆As₂F₆MoO₅**
 (CH₃)₂AsAs(CF₃)₂Mo(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.4.3
- C₉H₆CrF₆O₅P₂**
 (CH₃)₂PP(CF₃)₂Cr(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.3.2.3
- C₉H₆CrO₃**
 h⁶-C₆H₆Cr(CO)₃
 Exchange with C₂H₅OD in presence of [OD]⁻: 1.6.7.2.1
- C₉H₆F₄FeO₂**
 h⁷-C₅H₅Fe(CO)₂C₂F₄H
 Formation: 1.6.4.1.4
- C₉H₆F₆MoO₅P₂**
 (CH₃)₂PP(CF₃)₂Mo(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.3.2.3
- C₉H₇F₈OP**
 C₆H₅P[OCH(CF₃)₂]F₂H
 Formation: 1.5.3.2.3
- C₉H₇MnO₃**
 C₅H₄CH₃-h⁵Mn(CO)₃
 Reaction with R(+)-SiHMePh(1-C₁₀H₇): 1.10.5.4
 h⁵-C₅H₅CH₃Mn(CO)₃
 Formation: 1.6.4.1.4
- C₉H₉O₃Re**
 h⁵-C₅H₅(OC)₂Re=C(OH)CH₃
 Formation by protonation of an acyl anion: 1.10.6.2.1
- C₉H₁₀**
 C₆H₅C(CH₃)=CH₂
 Reaction with HMn(CO)₅: 1.6.4.1.4
 Reaction with CH₃SiCl₂H: 1.6.4.1.4
- C₆H₅CH₂CH=CH₂**
 Electrochemical reduction: 1.6.3.1.3
- C₉H₁₁CoN₂O₂**
 h⁵-C₅H₅Co(ON)₂C₂(CH₃)₂
 Reduction by Li[AlH₄]: 1.5.5.1
- C₉H₁₂**
 C₆H₅CH(CH₃)₂
 Formation: 1.6.4.1.4
 C₆H₇CH₂CHCH₂
 Formation: 1.6.3.1.3
- C₉H₁₂Cl₂Si**
 C₆H₅C(CH₃)HCH₂SiCl₂H
 Formation: 1.6.4.1.4
- C₉H₁₂CrO₅P₂**
 (CH₃)₂PP(CH₃)₂Cr(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.3.2.3
- C₉H₁₂FeO**
 h⁵-C₅H₅Fe(CO)CH(CH₃)₂
 Formation: 1.6.5.1.4
- C₉H₁₂MoO₅P₂**
 (CH₃)₂PP(CH₃)₂Mo(CO)₅
 Reaction with (CH₃)₃SnH: 1.5.3.2.3
- C₉H₁₄AsGe**
 (CH₃)₃GeAsH(C₆H₅)
 Redistribution: 1.5.4.3
- C₉H₁₄AsSi**
 (CH₃)₃SiAsH(C₆H₅)
 Redistribution: 1.5.4.3
- C₉H₁₄PSi**
 (CH₃)₃SiP(H)C₆H₅
 Cleavage by CH₃OH: 1.5.3.2.3
 Formation: 1.5.3.2.3
- C₉H₁₆BF₄MoN₃O₃**
 [Mo(CH₂CH₂NH)₃(CO)₃H][BF₄]
 Equilibrium acidity at metal: 1.10.6.1.2
- C₉H₁₈BD₃**
 (CH₃CH₂CHD)₃B
 Formation: 1.6.7.1.1
- C₉H₁₉N₄P**
 [(CH₂)₂]₃(CH₂)₃N₄PH
 Formation: 1.5.3.2.3
- C₉H₂₁B**
 (CH₃CH₂CH₂)₃B
 Formation: 1.6.4.1.4
- C₉H₂₁BO₃**
 B[(CH₃)₂CHO]₃
 Reduction: 1.7.3.2
 B(OC₃H₇-i)₃
 Reduction with NaAlH₄: 1.7.5.1
 B(OC₃H₇)₃
 Formation: 1.6.4.1.2
 Reaction with H₂O: 1.6.4.1.2
 Reduction: 1.7.3.2

- C₉H₂₁ClGeMg**
(i-C₃H₇)₃GeMgCl
Hydrolysis: 1.6.3.3.1
- C₉H₂₁ClPb**
(C₃H₇)₃PbCl
Reduction with (C₂H₅)₂AlH: 1.6.4.5.1
(i-C₃H₇)₃PbCl
Reduction by LiAlH₄: 1.6.5.5
- C₉H₂₁ClSn**
(n-C₃H₇)₃SnCl
Reduction by LiAlH₄: 1.6.5.4.1
- C₉H₂₁DSi**
(i-C₃H₇)₃SiD
Formation: 1.6.7.1.2
- C₉H₂₁GeP**
(C₂H₅)₂GeC₃H₆PC₂H₅
Cleavage by protonic acids: 1.5.3.2.3
- C₉H₂₁NSSi**
(C₂H₅)₃SiN(C₂H₅)CHS
Formation: 1.6.4.1.3
- C₉H₂₁O₃P**
(i-C₃H₇O)₃P
Hydrolysis in CH₃CN: 1.5.3.2.3
Protonation in strong acid: 1.5.3.2.2, 1.5.3.2.3
CH₃P(O)(OC₄H₉-n)₂
Formation: 1.5.3.2.2
CH₃P(O)(OC₄H₉-t)₂
Formation: 1.5.3.2.2
- C₉H₂₂BKO₃**
KBH[OCH(CH₃)₂]₃
Formation: 1.7.4.1.2
- C₉H₂₂ClGeP**
(C₂H₅)₂Ge(Cl)CH₂CH₂CH₂P(H)C₂H₅
Formation: 1.5.3.2.3
- C₉H₂₂Ge**
(i-C₃H₇)₃GeH
Formation: 1.6.3.3.1, 1.6.4.3.1
- C₉H₂₂N₄**
(NH)₄[(CH₂)₂]₃[(CH₂)₃]
Reaction with [(CH₃)₂N]₃P: 1.5.3.2.3
- C₉H₂₂P₂**
(n-C₄H₉)₂C(PH₂)₂
Formation: 1.5.5.2.1
- C₉H₂₂Pb**
(C₃H₇)₃PbH
Formation: 1.6.4.5.1
(i-C₃H₇)₃PbH
Formation: 1.6.5.5
(n-C₃H₇)₃PbH
Formation: 1.6.4.5.2
- C₉H₂₂Si**
(i-C₃H₇)₃SiH
Formation: 1.6.5.2.2
- C₉H₂₂Sn**
(i-C₃H₇)₃SnH
Formation: 1.6.4.4.2
(n-C₃H₇)₃SnH
Formation: 1.6.4.4.3, 1.6.5.4.1
- C₉H₂₃GeP**
C₃H₇(CH₃)Ge(CH₃)P(C₂H₅)₂
Cleavage by LiAlH₄: 1.5.5.2.3
- C₉H₂₄Si₃**
[(CH₃)₂SiCH₂]₃
Formation: 1.6.4.2.3
- C₉H₂₅BPb**
(n-C₃H₇)₃Pb(BH₄)
Reaction with CH₃OH: 1.6.4.5.2
- C₉H₂₇AsSi₃**
[(CH₃)₃Si]₃As
Cleavage by protonic acids: 1.5.3.3.3
- C₉H₂₇BiGe₃**
[(CH₃)₃Ge]₃Bi
Hydrolysis: 1.5.3.5
- C₉H₂₇Cl₄P₃W**
WCl₄(PMe₃)₃
Reaction with LiAlH₄: 1.10.7.3
- C₉H₂₇NPSi₃**
[(CH₃)₃Si]₃NPSi(CH₃)₃
Cleavage by LiAlH₄: 1.5.5.2.3
- C₉H₂₇N₂PSi₃**
[(CH₃)₃Si]₃NPNSi(CH₃)₃
Reaction with secondary amines: 1.5.3.2.3
- C₉H₂₇SbSn₃**
[(CH₃)₃Sn]₃Sb
Reaction with (CH₃)₃SnH: 1.6.4.3.3
- C₉H₂₈Cl₄IrP₃**
[Me₃PH][IrCl₄(PMe₃)₂]
Reaction with LiAlH₄: 1.10.7.2
- C₉H₂₉N₂PSi₃**
[(CH₃)₃Si]₂NP(H)N(H)Si(CH₃)₃
Formation: 1.5.5.2.3
- C₉H₃₃P₃W**
WH₆(PMe₃)₃
Formation from LiAlH₄: 1.10.7.3
- C₁₀HCr₇KO₁₀**
K[HCr₇(CO)₁₀]
Formation: 1.10.9
- C₁₀HIO₁₀Os₃**
Os₃HI(CO)₁₀
Formation: 1.10.5.1
- C₁₀HNO₁₁Ru₃**
HRu₃(CO)₁₀NO
Kinetic product of protonation of anion: 1.10.6.2.4
Thermodynamic product of protonation of anion: 1.10.6.2.4

- C₁₀H₂F₁₂Fe₂O₆P₂**
H(CO)₃Fe[μ-P(CF₃)₂]₂FeH(CO)₃μ
Formation: 1.10.5.2
- C₁₀H₂O₁₀Os₃**
H₂Os₃(CO)₁₀
Formation: 1.10.3.1, 1.10.3.2, 1.10.4.3.4
Reaction with C₆H₅CHNCH₃: 1.5.4.1.2
- C₁₀H₅F₃O₅W**
h⁵-C₅H₅W(CO)₃O₂CCF₃
Formation by diprotonation and loss of hydrogen: 1.10.6.1.1
- C₁₀H₆F₃NO₈Os₃**
H(μ₂-H)₃Os₃(CO)₈(μ₃-NCH₂CF₃)
Formation: 1.10.4.3.4
- C₁₀H₇D**
Formation: 1.6.7.1.1
- C₁₀H₇Na**
Reaction with DCl: 1.6.7.1.1
Reaction with H₂O: 1.6.2.5
- C₁₀H₇Na**
NaC₁₀H₇
Reduction of (C₂H₅)₂TiCl₂: 1.5.3.1.3
- C₁₀H₈**
Formation: 1.6.2.5
Isomerization: 1.6.6.1
Thermal isomerization: 1.6.4.1.5
- C₁₀H₉FeNO₂**
h⁵-C₅H₅(CO)₂FeCH(CH₃)CN
Protonation: 1.5.3.1.3
- C₁₀H₁₀ClMgN₂Ti**
(h⁵-C₅H₅)₂TiN₂MgCl
Methanolysis: 1.5.3.1.3
- C₁₀H₁₀ClOP**
(C₆H₄)C₃H₃(CH₃)P(O)Cl
Reduction by LiAlH₄: 1.5.5.2.1
- C₁₀H₁₀Cl₂Nb**
(h⁵-C₅H₅)₂NbCl₂
Reaction with alkoxyaluminum hydrides: 1.10.7.4
Reaction with borohydride: 1.10.9
- C₁₀H₁₀Cl₂Zr**
(h⁵-C₅H₅)₂ZrCl₂
Reaction with alkoxyaluminum hydrides: 1.10.7.4
Reaction with borohydride: 1.10.9
- C₁₀H₁₀Fe**
(h⁵-C₅H₅)₂Fe
Protonation at metal: 1.10.6.1.1
- C₁₀H₁₀FeNO₂**
h⁵-C₅H₅(CO)₂Fe[(μ₂-CH₃(H)*C=CNH)]⁺
Formation: 1.5.3.1.3
- C₁₀H₁₀FeO₂**
- C₁₀H₁₂Zr**
(h⁵-C₅H₅)₂ZrH₂
Reaction with (h⁵-C₅H₅)₂WCO:
1.6.4.1.2
[(h⁵-C₅H₅)₂ZrH₂]_n
Formation: 1.10.9
- C₁₀H₁₃N₂OP**
C₆H₄O(NH)PN(CH₂CH₂)₂
Reaction with diols: 1.5.3.2.3
- C₁₀H₁₃Nb**
(h⁵-C₅H₅)₂NbH₃
Catalyst in D₂ exchange with C₆H₆:
1.6.7.2.1
Formation: 1.10.3.2, 1.10.4.3.1, 1.10.7.4
- C₁₀H₁₃Ta**
(h⁵-C₅H₅)₂TaH₃
Formation: 1.10.4.3.1, 1.10.9
- C₁₀H₁₄BNb**
(h⁵-C₅H₅)₂NbBH₄
Reaction with PMe₂Ph: 1.10.9
- C₁₀H₁₄ClOP**
n-C₄H₉(C₆H₅)P(O)Cl
Reduction with HSiCl₃: 1.5.4.2.2
- C₁₀H₁₄NO₂P**
C₆H₅P(H)(OCH₂CH₂)₂N
Reaction with (h⁵-C₅H₅)Mo(CO)₃Cl:
1.5.3.1.3
- C₁₀H₁₄NO₃P**
C₆H₄O(NH)PH(C₂H₅)OCOCH₃
Formation: 1.5.3.2.3
- C₁₀H₁₅Co**
HCo(1,3-pentadiene)₂
Formation: 1.10.2
- C₁₀H₁₅OP**
t-C₄H₉(C₆H₅)P(O)H
Formation: 1.5.2.2
- C₁₀H₁₅O₂PW**
h⁵-C₅H₅W(CO)₂(PMe₃)H
Equilibrium acidity: 1.10.6.2.2
- C₁₀H₁₅O₃P**
C₆H₅P(O)(OC₂H₅)₂
Reduction by LiAlH₄: 1.5.5.2.2
Reduction with (C₆H₅)₂SiH₂ or HSiCl₃:
1.5.4.2.2
- C₁₀H₁₆NO₂P**
C₆H₄O(NH)PH(C₂H₅)OC₂H₅
Formation: 1.5.3.2.3
- C₁₀H₁₇N₂PS**
C₆H₅P(S)(NHC₂H₅)₂
Redistribution: 1.5.4.1.3
- C₁₀H₁₇PSn**
(CH₃)₃SnCH₂P(H)C₆H₅
Formation: 1.5.5.2.2

- C₁₀H₁₈B₂Zr**
(h⁵-C₅H₅)₂Zr(BH₄)₂
Formation: 1.10.9
- C₁₀H₁₉Sb**
(n-C₄H₉)₂SbCCH
Reaction with (C₆H₅)₃SnH: 1.5.4.4
- C₁₀H₂₂O₃Sn**
[(i-C₃H₇)₃Sn][CO₃H]
Thermolysis: 1.6.4.4.2
- C₁₀H₂₄N₂**
(C₂H₅)₂C(NH₂)C(NH₂)(C₂H₅)₂
Formation: 1.5.5.1
- C₁₀H₂₄N₄**
cyclo-(NHCH₂CH₂)₄
Reaction with [(CH₃)₂N]₃P: 1.5.3.2.3
- C₁₀H₂₄O₆P₂**
(C₂H₅O)₂P(O)(CH₂)₂P(O)(OC₂H₅)₂
Reduction by LiAlH₄: 1.5.5.2.2
- C₁₀H₂₅GeP**
(C₂H₅)₃GeP(C₂H₅)₂
Reaction with C₆H₅NH₂: 1.5.3.2.3
- C₁₀H₂₅N₃Sn**
(C₂H₅)₃SnN(C₂H₅)₂
Reaction with (C₆H₅)₃GeH: 1.5.4.1.3
Reaction with (C₆H₅)₃SnH: 1.5.4.1.3
Reduction by B₂H₆ or (C₄H₉)₂AlH:
1.6.4.4.3
- C₁₀H₂₆N₂Sn**
(CH₃)₂Sn[N(C₂H₅)₂]₂
Reduction by B₂H₆ or (C₄H₉)₂AlH:
1.6.4.4.3
- C₁₀H₂₆Sn₂**
H(n-C₄H₉)₂SnSn(CH₃)₂H
Formation: 1.6.4.4.3
- C₁₀H₂₇AsSi₂**
(CH₃)₃CAs[Si(CH₃)₃]₂
Thermolysis of [(CH₃)₃Si]₂AsH: 1.5.4.3
- C₁₀H₂₇BN₂Sn**
(C₂H₅)₃SnB[N(CH₃)₂]₂
Hydrolysis: 1.6.3.4.1
- C₁₀H₂₇N₂PSSi₂**
(CH₃)₃SiN[Si(CH₃)₃]₂P(S)NC₄H₉-t
Methanolysis: 1.5.3.1.3
- C₁₀H₂₇N₂PSi₂**
[(CH₃)₃Si]₂NPNC₄H₉-t
Reaction with secondary amines:
1.5.3.2.3
- C₁₀H₂₈N₄Zn₂**
[HZnCH₃NCH₂CH₂N(CH₃)₂]₂
Formation: 1.9.4.1, 1.9.4.2
- C₁₀H₃₀Li₂Si₅**
Li₂[(CH₃)₂Si]₅
Hydrolysis: 1.6.3.2.1
- C₁₀H₃₂Si₅**
H₂[(CH₃)₂Si]₅
Formation: 1.6.3.2.1
- C₁₀H₄₆N₃PSi₄**
{[(CH₃)₃Si]₂N}₂P(H)NC₄H₉-t
Formation: 1.5.3.2.3
- C₁₀Mn₂O₁₀**
Mn₂(CO)₁₀
Reaction with H₂: 1.10.3.2
- C₁₀O₁₀Re₂**
Re₂(CO)₁₀
Hydrolysis: 1.10.5.6.1
Reaction with NaBH₄: 1.10.9
Reaction with H₂: 1.10.3.2
Reaction with alkoxyborohydride:
1.10.7.2
- C₁₁H₂O₁₁Ru₃**
H₂Ru₃(CO)₁₁
Rearrangement: 1.10.6.2.4
- C₁₁H₂O₁₂Os₃**
Os₃(μ-H)(μ-O₂CH)(CO)₁₀
Formation: 1.10.5.6.1
- C₁₁H₄F₃NO₉Os₃**
(μ₂-H)₂Os₃(CO)₉(μ₃-NCH₂CF₃)
Reaction with H₂: 1.10.4.3.4
- C₁₁H₄O₉Os₃**
H₂Os₃(CO)₉C≡CH₂
Protonation at metal-metal bond:
1.10.6.1.4
- C₁₁H₄O₁₁Os₃**
Os₃H(OCH₃)(CO)₁₀
Formation: 1.10.5.6.1
- C₁₁H₆Fe₃O₁₀**
H₃Fe₃(μ₃-COCH₃)(CO)₉
Formation: 1.10.4.3.4
- C₁₁H₆O₁₀Os₃**
H₃Os₃(μ₃-COCH₃)(CO)₉
Formation: 1.10.3.2, 1.10.4.3.4
- C₁₁H₆O₁₀Ru₃**
H₃Ru₃(μ₃-COCH₃)(CO)₉
Formation: 1.10.3.2, 1.10.4.3.3
- C₁₁H₈MoO₃**
(C₈H₈)Mo(CO)₃
Protonation: 1.6.3.1.3
- C₁₁H₁₀OW**
(h⁵-C₅H₅)₂WCO
Reaction with (h⁵-C₅H₅)₂ZrH₂: 1.6.4.1.2
- C₁₁H₁₁ClOZr**
(h⁵-C₅H₅)₂Zr(Cl)CHO
Formation: 1.6.4.1.2
- C₁₁H₁₁F₇N₂PW**
[(h⁵-C₅H₅)W(H₂NNC₆H₄F-p)][PF₆]
Formation: 1.5.4.1.2

- C₁₁H₁₁NbO**
(h⁵-C₅H₅)₂Nb(CO)H
Reaction with H₂: 1.10.4.3.1
- C₁₁H₁₁OTa**
(h⁵-C₅H₅)₂Ta(CO)H
Reaction with H₂: 1.10.4.3.1
- C₁₁H₁₂F₆N₂PW**
(h⁵-C₅H₅)W(H₂NNC₆H₅)[PF₆]
Formation: 1.5.4.1.2
- C₁₁H₁₂W**
C₆H₆WHC₅H₅-h⁵
Formation: 1.1.10.2
- C₁₁H₁₃ClZr**
CH₃(h⁵-C₅H₅)₂Zr(Cl)
Reaction with H₂O: 1.6.3.1.3
- C₁₁H₁₃IW**
(h⁵-C₅H₅)₂W(CH₃)I
Reaction with alkoxyaluminum hydrides: 1.10.7.4
- C₁₁H₁₃Rh**
h⁵-C₅H₅RhC₆H₈-1,3-h⁴
Protonation at metal: 1.10.6.1.1
- C₁₁H₁₄F₆PRh**
[h⁵-C₅H₅RhH(h⁴-1,3-C₆H₈)] [PF₆]
Exchange between metal hydride and endo protons: 1.10.6.1.1
- C₁₁H₁₄NO₃P**
C₆H₄O(NH)PH(C₂H₅)OCOCHCH₂
Formation: 1.5.3.2.3
- C₁₁H₁₄OZr**
(h⁵-C₅H₅)₂ZrH(OCH₃)
Formation: 1.6.2.1.2
- C₁₁H₁₄W**
(h⁵-C₅H₅)₂W(H)CH₃
Formation: 1.10.7.4
- C₁₁H₁₅CoN₂O₂**
h⁵-C₅H₅Co(ON)₂C₂(C₂H₅)₂
Reduction by Li[AlH₄]: 1.5.5.1
- C₁₁H₁₅D₂N**
(C₂H₅)₂CDNDC₆H₅
Formation: 1.5.7.1.1
- C₁₁H₁₅N**
(C₂H₅)₂CNC₆H₅
Reduction by Li[AlD₄]: 1.5.7.1.1
- C₁₁H₁₅NO**
C₆H₅CON(C₂H₅)₂
Reduction with Li[AlD₄]: 1.6.7.1.1
- C₁₁H₁₆NOP**
C₄H₈N(CH₃)P(O)C₆H₅
Reduction by Li[AlH₄]: 1.5.5.2.2
- C₁₁H₁₇NP**
C₄H₈N(CH₃)PHC₆H₅
Formation: 1.5.5.2.2
- C₁₁H₁₇O₃P**
C₆H₅CH₂P(O)(OC₂H₅)₂
Reduction by Li[AlH₄]: 1.5.5.2.2
- C₁₁H₁₈OOs**
[h⁵-C₅(CH₃)₅]Os(CO)H₃
Formation: 1.10.4.3.4
- C₁₁H₁₈O₃P₂**
C₆H₅P(H)CH₂P(O)(OC₂H₅)₂
Reduction by Li[AlH₄]: 1.5.5.2.2
- C₁₁H₂₀**
n-C₇H₁₅CHCHCHCH₂
Reaction with (i-C₄H₉)₂AlH: 1.6.4.1.4
- C₁₁H₂₃CoP₂**
h⁵-C₅H₅Co(PMe₃)₂
Equilibrium basicity at metal: 1.10.6.1.1
Oxidation on diprotonation: 1.10.6.1.1
- C₁₁H₂₃NiPSi₂**
h⁵-C₅H₅NiP[Si(CH₃)₃]₂
Methanolysis: 1.5.3.2.3
- C₁₁H₂₄CoF₆P₃**
[h⁵-C₅H₅Co(PMe₃)₂H] [PF₆]
Formation by metal protonation: 1.10.6.1.1
- C₁₁H₂₆N₄**
(NH)₄[(CH₂)₂][(CH₂)₃]₃
Reaction with [(CH₃)₂N]₃P: 1.5.3.2.3
- C₁₁H₂₆OSi**
(i-C₃H₇)₃SiOC₂H₅
Reduction by LiAlH₄: 1.6.5.2.2
- C₁₁H₂₆O₄Si**
(i-C₃H₇O)₃SiOC₂H₅
Reduction with LiAlD₄: 1.6.7.1.2
- C₁₁H₂₇NPSSi**
(CH₃)₃SiN[C(CH₃)₃]P(S)(C₄H₉-t)
Methanolysis: 1.5.3.1.3
- C₁₁H₂₇OPSi**
(CH₃)₃SiPC[OSi(CH₃)₃](t-C₄H₉)
Reaction with alcohols: 1.5.3.2.3
- C₁₁H₂₇P₃Si**
(t-C₄H₉P)₂PSi(CH₃)₃
Methanolysis: 1.5.3.2.3
- C₁₁H₃₁N₂OPSSi₂**
(CH₃)₃SiN[Si(CH₃)₃]P(S)(OCH₃)NH(t-C₄H₉)
Formation: 1.5.3.1.3
- C₁₂Co₃NaO₁₂Os**
Na[OsCo₃(CO)₁₂]
Protonation on metal core: 1.10.6.2.4

- C₁₂D₄O₁₂Ru₄**
 D₄Ru₄(CO)₁₂
 Formation: 1.10.4.3.3
- C₁₂F₁₀Zn**
 (C₆F₅)₂Zn
 Forms Na₂[ZnH(C₆F₅)₂]₂ with NaH:
 1.9.4.1
- C₁₂FeO₁₂Ru₂**
 FeRu₂(CO)₁₂
 Reaction with H₂: 1.10.4.3.3
- C₁₂Fe₃O₁₂**
 Fe₃(CO)₁₂
 Reaction with alkanethiols: 1.10.5.6.2
- C₁₂HCO₃FeO₁₂**
 HFeCo₃(CO)₁₂
 Formation by protonation of metal
 core: 1.10.6.2.4
- C₁₂HCO₃O₁₂Os**
 HOsCo₃(CO)₁₂
 Formation by protonation of metal
 core: 1.10.6.2.4
- C₁₂HF₆O₁₂Os₃P**
 [HOs₃(CO)₁₂][PF₆]
 Formation by protonation of a metal-
 metal bond: 1.10.6.1.4
- C₁₂HFe₄NO₁₂**
 HFe₄N(CO)₁₂
 Formation by protonation of metal
 core: 1.10.6.2.4
- C₁₂HMnO₁₂Os₂**
 HMnOs₂(CO)₁₂
 Formation by protonation of metal
 core: 1.10.6.2.4
- C₁₂H₂Co₂O₁₂Ru₂**
 H₂Ru₂Co₂(CO)₁₂
 Formation: 1.10.4.3.3
- C₁₂H₂D₂O₁₂Ru₄**
 H₂D₂Ru₄(CO)₁₂
 Formation: 1.10.4.3.3
- C₁₂H₂F₃NO₁₀Os₃**
 HOs₃(CO)₁₀NCHCF₃
 Reaction with H₂: 1.5.2.1.2
- C₁₂H₂O₁₁Os₃**
 Os₃(CO)₁₁CH₂
 Formation: 1.6.3.1.3
- C₁₂H₃BFe₄O₁₂**
 Fe₄H(BH₂)(CO)₁₂
 Formation: 1.10.5.2
- C₁₂H₃BO₁₂Ru₄**
 Ru₄H(BH₂)(CO)₁₂
 Formation: 1.10.5.2
- C₁₂H₃CoO₁₂Ru₃**
 H₃CoRu₃(CO)₁₂
 Formation: 1.10.4.3.3
- C₁₂H₃Co₃O₁₀**
 Co₃(CO)₉CCOCH₃
 Reaction with (C₂H₅)₃SiH: 1.6.4.1.2
- C₁₂H₃O₁₂Re₃**
 H₃Re₃(CO)₁₂
 Formation: 1.10.9
- Re₃H₃(CO)₁₂**
 Formation: 1.10.3.2
- C₁₂H₄F₃NO₁₀Os₃**
 HOs₃(CO)₁₀HNCH₂CF₃
 Formation: 1.5.2.1.2
- C₁₂H₄FeO₁₂Os₃**
 H₄FeOs₃(CO)₁₂
 Formation: 1.10.4.3.4
- C₁₂H₄FeO₁₂Ru₃**
 H₄FeRu₃(CO)₁₂
 Equilibrium acidity and rate of forma-
 tion by protonation of an anion:
 1.10.6.2.4
 Formation: 1.10.3.2, 1.10.4.3.3
- C₁₂H₄Fe₃O₁₁**
 HFe₃(μ-COCH₃)(CO)₁₀
 Reaction with H₂ and SbPh₃: 1.10.3.2
 Reaction with H₂: 1.10.4.3.4
- C₁₂H₄O₁₁Os₃**
 HOs₃(μ-COCH₃)(CO)₁₀
 Reaction with H₂: 1.10.3.2, 1.10.4.3.4
- C₁₂H₄O₁₁Ru₃**
 HRu₃(μ-COCH₃)(CO)₁₀
 Reaction with H₂: 1.10.3.2, 1.10.4.3.3
- C₁₂H₄O₁₂Os₄**
 H₄Os₄(CO)₁₂
 Equilibrium acidity and rate of forma-
 tion by protonation of an anion:
 1.10.6.2.4
 Formation: 1.10.3.2
- C₁₂H₄O₁₂Re₄**
 H₄Re₄(CO)₁₂
 Formation: 1.10.3.2
- C₁₂H₄O₁₂Ru₄**
 H₄Ru₄(CO)₁₂
 Equilibrium acidity and rate of forma-
 tion by protonation of an anion:
 1.10.6.2.4
 Formation: 1.10.6.2.4, 1.10.3.2, 1.10.4.3.3,
 1.10.9

- C₁₂H₄O₁₆Re₄**
 Re(OH)₄(CO)₁₂
 Formation: 1.10.5.6.1
- C₁₂H₅Co₃O₉**
 Co₃(CO)₉CCH₂CH₃
 Formation: 1.6.4.1.2
- C₁₂H₆O₁₀Os₃S**
 HO₃(CO)₁₀SC₂H₅
 Formation: 1.10.5.6.2
- C₁₂H₆O₁₀Ru₃S**
 HRu₃(SC₂H₅)(CO)₁₀
 Formation: 1.10.5.6.2
- C₁₂H₈Cl₂NO₄PS**
 C₆H₄O₂P(Cl)NSO₂C₆H₄Cl
 Reaction with 1,2-(HO)₂C₆H₄: 1.5.3.1.3
- C₁₂H₉N₃**
 C₆H₅C₆H₄N₃
 Reaction with H₂: 1.5.2.1.2
- C₁₂H₁₀BiCl**
 (C₆H₅)₂BiCl
 Reduction by Li[AlH₄]: 1.5.5.5
- C₁₂H₁₀Br₂Ge**
 (C₆H₅)₂GeBr₂
 Reduction by Li[AlH₄]: 1.6.5.3.1
- C₁₂H₁₀ClOP**
 (C₆H₅)₂P(O)Cl
 Reduction by Li[AlH₄]: 1.5.5.2.1
- C₁₂H₁₀CIP**
 (C₆H₅)₂PCl
 Hydrolysis: 1.5.6.2
 Reduction by Na[(CH₃OCH₂CH₂O)₂]
 AlH₂]: 1.5.5.2.1
 Reduction by metals: 1.5.6.2
 Reduction by (C₆H₅)₂SiH₂ or HSiCl₃:
 1.5.4.2.2
- C₁₂H₁₀ClSb**
 (C₆H₅)₂SbCl
 Reduction by Li[BH₄]: 1.5.5.4
- C₁₂H₁₀Cl₂Ge**
 (C₆H₅)₂GeCl₂
 Electrochemical reduction in H₂O:
 1.6.3.3.1
 Redistribution with germanes: 1.6.4.3.1
- C₁₂H₁₀Cl₂Si**
 (C₆H₅)₂SiCl₂
 Reduction by Li[AlH₄]: 1.6.5.2.1
- C₁₂H₁₀Cl₂Sn**
 (C₆H₅)₂SnCl₂
 Electrolytic reduction to (C₆H₅)₂SnH₂:
 1.6.3.4.1
 Reduction by Li[AlH₄]: 1.6.5.4.1
- Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
- C₁₂H₁₀Cl₃P**
 (C₆H₅)₂PCl₃
 Reduction by Li[AlH₄]: 1.5.5.2.1
- C₁₂H₁₀DP**
 (C₆H₅)₂PD
 Formation: 1.5.7.1.2
- C₁₂H₁₀D₂Si**
 (C₆H₅)₂SiD₂
 Reduction of halophosphines: 1.5.7.1.2
- C₁₂H₁₀LiP**
 (C₆H₅)₂PLi
 Reaction with D₂O: 1.5.7.1.2
- C₁₂H₁₀LiSb**
 (C₆H₅)₂SbLi
 Reaction with H₂O: 1.5.3.4
- C₁₂H₁₀NaP**
 Na[(C₆H₅)₂P]
 Protonation to (C₆H₅)₂PH: 1.5.3.2.2
- C₁₂H₁₀Ni₂O₂**
 Ni₂(C₅H₅)₂(CO)₂
 Reaction with H₂ and Os₃(CO)₁₂:
 1.10.3.2
- C₁₂H₁₀O₂Ti**
 (h⁵-C₅H₅)₂Ti(CO)₂
 Reaction with H₂: 1.6.2.1.2
- C₁₂H₁₀O₂Zr**
 (h⁵-C₅H₅)₂Zr(CO)₂
 Reaction with H₂: 1.6.2.1.2
- C₁₂H₁₁As**
 (C₆H₅)₂AsH
 Formation: 1.5.3.3.3, 1.5.4.3, 1.5.5.3.1,
 1.5.6.3
- C₁₂H₁₁BrSn**
 (C₆H₅)₂SnH(Br)
 Formation: 1.6.4.4.1
- C₁₂H₁₁ClGe**
 (C₆H₅)₂GeHCl
 Formation: 1.6.4.3.1
- C₁₂H₁₁ClSi**
 (C₆H₅)₂SiHCl
 Formation: 1.6.4.2.3, 1.6.4.3.1
- C₁₂H₁₁ClSn**
 (C₆H₅)₂SnHCl
 Formation: 1.6.3.4.3, 1.6.4.4.1
- C₁₂H₁₁FSn**
 (C₆H₅)₂SnHF
 Formation: 1.6.4.4.1
- C₁₂H₁₁N**
 C₆H₅C₆H₄NH₂
 Formation: 1.5.2.1.2, 1.9.4.2

C₁₂H₁₁NaZnNa[ZnH(C₆H₅)₂]From NaZnH(C₆H₅)₂ with (C₆H₅)₂Zn:

1.9.4.2

C₁₂H₁₁OP(C₆H₅)₂P(O)H

Formation: 1.5.3.2.3

Industrial formation: 1.5.6.2

C₁₂H₁₁O₂P(C₆H₅)₂P(O)OHReduction by LiAlH₄: 1.5.5.2.2**C₁₂H₁₁O₃P**(C₆H₅)₂P(O)H

Formation: 1.5.3.2.2

C₁₂H₁₁P(C₆H₅)₂PH

Formation: 1.5.3.2.1, 1.5.3.2.2, 1.5.3.2.3,

1.5.5.2.1, 1.5.5.2.2, 1.5.5.2.3

Industrial formation: 1.5.6.2

C₁₂H₁₁Sb(C₆H₅)₂SbH

Formation: 1.5.5.4

C₁₂H₁₂CrO₃h⁶-C₆H₃Me₃Cr(CO)₃

Protonation at metal: 1.10.6.1.1

C₁₂H₁₂Ge(C₆H₅)₂GeH₂

Exchange with halogermenes: 1.6.4.3.1

Formation: 1.6.3.3.1, 1.6.4.3.3, 1.6.5.3.1

C₁₂H₁₂MoO₂h⁵-C₅H₅Mo(CO)₂C₃H₇-h³

Formation: 1.10.5.3

C₁₂H₁₂Os₃Os₃(CO)₁₂Reaction with H₂: 1.10.3.2**C₁₂H₁₂P₂**(C₆H₅PH)₂

Formation: 1.5.4.2.4

C₁₂H₁₂Si(C₆H₅)₂SiH₂

Formation: 1.6.4.2.3, 1.6.5.2.1, 1.6.5.2.2

Reaction with C₅H₁₀P(O)OH: 1.5.4.2.2Reduction of GeCl₄: 1.6.4.3.1

Reduction of chlorophosphines: 1.5.4.2.2

C₁₂H₁₂Sn(C₆H₅)₂SnH₂

Exchange reaction with dihalostannanes: 1.6.4.4.1

Formation: 1.6.3.4.1, 1.6.4.4.1, 1.6.4.4.2,

1.6.4.4.3, 1.6.5.4.1

Reaction with (C₂H₅)₃SnN(C₆H₅)COH:

1.5.4.1.3

Reaction with CH₃OH: 1.6.3.4.3**C₁₂H₁₃N₂PS**(C₆H₅)₂P(S)NHNH₂

Redistribution: 1.5.4.1.3

C₁₂H₁₄WC₆H₅CH₃WHC₃H₅-h⁵

Formation: 1.10.2

C₁₂H₁₅F₆N₂PW[(h⁵-C₅H₅)W(H₂NNC₆H₅CH₃-p)][PF₆]

Formation: 1.5.4.1.2

C₁₂H₁₅IrO₂Ir(C₅Me₅-h⁵)(CO)₂

Reaction with cyclohexane: 1.10.5.3

C₁₂H₁₅KO₂RuK[h⁵-C₅(CH₃)₅Ru(CO)₂]

Protonation at metal: 1.10.6.2.1

C₁₂H₁₅O₂Rhh⁵-C₅(CH₃)₅Rh(CO)₂

Reaction with acid to give a dinuclear

complex: 1.10.6.1.4

C₁₂H₁₅O₃PC₆H₅CCP(O)(OC₂H₅)₂Reduction of LiAlH₄: 1.5.5.2.2**C₁₂H₁₅O₄P**CH₃(C₆H₅)P(H)C(CO₂CH₃)₂Tautomeric exchange with CH₃(C₆H₅)*PCH(CO₂CH₃)₂: 1.5.3.2.3CH₃(C₆H₅)P(H)(CCO₂CH₃)₂Tautomeric exchange with CH₃(C₆H₅)*P(H)C(CO₂CH₃)₂: 1.5.3.2.3**C₁₂H₁₆BF₄IrO₂**[h⁵-C₅(CH₃)₅Ir(CO)₂H][BF₄]

Formation by metal protonation:

1.10.6.1.1

C₁₂H₁₆NO₃PN[CH₂C(CH₃)O]₂PH(OC₆H₅)

Formation in d,l- and meso-forms:

1.5.3.2.3

C₁₂H₁₆O₂Os[h⁵-C₅(CH₃)₅]Os(CO)₂HReaction with H₂: 1.10.4.3.4**C₁₂H₁₆O₂Ru**h⁵-C₅(CH₃)₅Ru(CO)₂H

Formation by protonation of a metal

anion: 1.10.6.2.1

C₁₂H₁₆Ti(h⁵-C₅H₅)₂Ti(CH₃)₂

Reaction with DCl: 1.6.7.1.1

C₁₂H₁₇Ta(h⁵-C₅H₄CH₃)₂TaH₃

Formation: 1.10.7.2

- C₁₂H₁₈NO₃P**
 $C_6H_4O(NH)P(H)O_2C_2(CH_3)_4$
 Formation: 1.5.3.2.3
- C₁₂H₂₀Sn**
 $(C_2H_5)_3SnC_6H_5$
 Reaction with aq base: 1.6.2.5
 Reaction with basic D₂O: 1.6.7.1.1
- C₁₂H₂₁MoO₃P₃**
 $(CH_2=CHCH_2PH_2)_3Mo(CO)_3$
 Radical initiated cyclization: 1.6.4.1.4
 $(CO)_3Mo[PH(CH_2)_3]_3$
 Formation: 1.6.4.1.4
- C₁₂H₂₁O₂PSn**
 $(CH_3)_3SnCH_2P(O)C_6H_5(OC_2H_5)$
 Reaction with Li[AlH₄]: 1.6.5.4.3
 Reduction by Li[AlH₄]: 1.5.5.2.2
- C₁₂H₂₂ClSb**
 $(C_6H_{11})_2SbCl$
 Reduction by Li[AlH₄]: 1.5.5.4
- C₁₂H₂₂Cl₂Pb**
 $(C_6H_{11})_2PbCl_2$
 Reduction by Li[AlH₄]: 1.6.5.5
- C₁₂H₂₂Sn**
 $(n-C_4H_9)_2Sn(CHCH)_2$
 Formation: 1.6.4.1.4
- C₁₂H₂₃As**
 $(C_6H_{11})_2AsH$
 Formation: 1.5.3.3.3, 1.5.5.3.1
- C₁₂H₂₃Cl₃NP₂Re**
 $ReCl_3(NPh)(PMe_3)_2$
 Reaction with Li[AlH₄]: 1.10.7.3
- C₁₂H₂₃NSi₂**
 $[(CH_3)_3Si]_2NC_6H_5$
 Methanolysis: 1.5.3.1.2
- C₁₂H₂₃O₂P**
 $(C_6H_{11})_2P(O)OH$
 Reduction by LiAlH₄: 1.5.5.2.2
- C₁₂H₂₃O₃P**
 $(C_6H_{11}O)_2P(O)H$
 Formation: 1.5.3.2.2
- C₁₂H₂₃P**
 $(C_6H_{11})_2PH$
 Formation: 1.5.5.2.2
- C₁₂H₂₃PSi₂**
 $[(CH_3)_3Si]_2PC_6H_5$
 Methanolysis: 1.5.3.2.3
- C₁₂H₂₃Sb**
 $(C_6H_{11})_2SbH$
 Formation: 1.5.5.4
- C₁₂H₂₅N₄P**
 $[(CH_2)_3]_4N_4PH$
 Formation: 1.5.3.2.3
- C₁₂H₂₇Al**
 $(i-C_4H_9)_3Al$
 Elimination of olefin: 1.7.3.3
- C₁₂H₂₇ClPb**
 $(n-C_4H_9)_3PbCl$
 Reduction by $(C_2H_5)_2AlH$: 1.6.4.5.1
- C₁₂H₂₇ClSn**
 $(n-C_4H_9)_3SnCl$
 Reduction by Li[AlH₄]: 1.6.6.4
 Reduction by Na[BH₄]: 1.6.5.4.1
- C₁₂H₂₇DSn**
 $(n-C_4H_9)_3SnD$
 Formation: 1.6.7.1.4
- C₁₂H₂₇LiSn**
 $(n-C_4H_9)_3SnLi$
 Reactions with protonic acids: 1.6.3.4.1
- C₁₂H₂₇NaSn**
 $Na[(n-C_4H_9)_3Sn]$
 Reactions with protonic acids: 1.6.3.4.1
- C₁₂H₂₇O₃P**
 $(n-C_4H_9O)_3P$
 Protonation in strong acid: 1.5.3.2.3
- C₁₂H₂₈AlLiO₃**
 $Li[(i-C_4H_9O)_3AlH]$
 Reduction of SnCl₄: 1.6.5.4.1
 Reduction of NO₂C₆H₄COCl: 1.6.5.1.1
- C₁₂H₂₈BK**
 $K[HB(C_4H_9-s)_3]$
 Formation: 1.7.4.1.3
- C₁₂H₂₈Cl₂Ge₂**
 $[(i-C_3H_7)_2GeCl]_2$
 Reduction by LiAlH₄: 1.6.5.3.1
- C₁₂H₂₈Cl₂Si₂**
 $(i-C_3H_7)_2ClSiCl(C_3H_7-i)_2$
 Reaction with Li[i-C₃H₇]: 1.6.4.2.1
- C₁₂H₂₈Ge**
 $(n-C_4H_9)_3GeH$
 Reaction with $(n-C_4H_9)_2SbCCH$: 1.5.4.4
 Reaction with $CH_2=CHCHO_2CH_3$: 1.6.4.1.4
 Reaction with $C_6H_5C\equiv CH$: 1.6.4.1.4
- C₁₂H₂₈NP**
 $(C_2H_5)_2PN(C_4H_9-t)_2$
 Reaction with H₂S: 1.5.3.2.3
- C₁₂H₂₈Pb**
 $(n-C_4H_9)_3PbH$
 Formation: 1.6.4.5.1, 1.6.4.5.2
- C₁₂H₂₈Sn**
 $(n-C_4H_9)_3SnH$
 Exchange with $(C_2H_5)_3PbCl$: 1.6.4.5.1
 Formation: 1.6.3.4.1, 1.6.4.4.1, 1.6.4.4.2, 1.6.4.4.3, 1.6.5.4.1
 Industrial synthesis: 1.6.6.4
 Reaction with $R_2SnCl_2SnCl_2$: 1.6.4.4.1
 Reaction with $C_6H_5CHNC_6H_5$: 1.6.4.1.3
 Reaction with alkyl halides: 1.6.4.1.1
 Reduction of $(CH_3O)_2PH$: 1.5.4.2.2

- C₁₂H₂₉NO₆P₂**
 [(n-C₃H₇O)₂P(O)]₂NH
 Formation: 1.5.3.1.3
- C₁₂H₂₉O₂PS₂Si**
 (C₂H₅O)₂P(S)SCH₂CH₂Si(C₂H₅)₃
 Formation: 1.6.4.1.4
- C₁₂H₃₀CdGe₂**
 [(C₂H₅)₃Ge]₂Cd
 Reaction with (C₂H₅)₃SnH: 1.6.4.3.3
 Reaction with CH₃CO₂H: 1.6.3.3.3
- C₁₂H₃₀Cl₂P₂Pt**
 trans-PtCl₂(PEt₃)₂
 Reaction with RMgCl: 1.10.8.4
 Reaction with N₂H₄: 1.10.8.2
 Reaction with KOH and Me₂CHOH: 1.10.8
- C₁₂H₃₀Ge₂**
 [(i-C₃H₇)₂GeH]₂
 Formation: 1.6.5.3.1
- C₁₂H₃₀HgSn₂**
 [(C₂H₅)₃Sn]₂Hg
 Exchange reaction with (C₆H₅)₃SnH: 1.6.4.4.3
- C₁₂H₃₀NP₂Re**
 ReH₆(NHPh)(PMe₃)₂
 Formation from LiAlH₄: 1.10.7.3
- C₁₂H₃₀N₂Sn**
 (C₂H₅)₂Sn[N(C₂H₅)₂]₂
 Reduction by B₂H₆ or (C₄H₉)₂AlH: 1.6.4.4.3
- C₁₂H₃₀N₃P**
 [(C₂H₅)₂N]₃P
 Reaction with C₆H₅NH₂: 1.5.3.1.3
- C₁₂H₃₀P₂Pt**
 Pt[P(C₂H₅)₃]₂
 Reaction with H₂: 1.10.4.1.2
- C₁₂H₃₀Si₂**
 [(i-C₃H₇)₂SiH]₂
 Formation: 1.6.4.2.1
- C₁₂H₃₀Sn₂**
 (C₂H₅)₃SnSn(C₂H₅)₃
 Reaction with H₂: 1.6.2.4
- C₁₂H₃₁BPb**
 [(n-C₄H₉)₃Pb][BH₄]
 Reaction with CH₃OH: 1.6.4.5.2
- C₁₂H₃₁BrP₂Pt**
 trans-HBrPt(PEt₃)₂
 Formation: 1.10.8.4
- C₁₂H₃₁ClP₂Pt**
 trans-HClPt(PEt₃)₂
 Formation: 1.10.8, 1.10.8.2, 1.10.8.4, 1.10.9
 HClPt(PEt₃)₂
 Formation: 1.10.9
 Reaction with C₆H₅CON₃: 1.5.4.1.2
- Reaction with C₆H₅N₃: 1.5.4.1.2
 Reaction with C₂H₄: 1.6.4.1.4
- C₁₂H₃₁IP₂Pt**
 trans-Pt(H)I[P(C₂H₅)₃]₂
 Reaction with (H₃Si)₃P: 1.5.4.2.2
- C₁₂H₃₁N₂OPSSI**
 (CH₃)₃SiN[C(CH₃)₃][P-(S)(OCH₃)NH(C₄H₉-t)]
 Formation: 1.5.3.1.3
- C₁₂H₃₁P₃Si**
 [(C₂H₅)₂P]₃SiH
 Protonation of (C₂H₅)₂PLi: 1.5.3.2.3
- C₁₂H₃₂Cl₂P₄Ta**
 TaCl₂(Me₂PCH₂CH₂PMe₂)₂
 Reaction with alkoxyaluminum hydrides: 1.10.7.4
- C₁₂H₃₂P₂Pt**
 H₂Pt[P(C₂H₅)₃]₂
 Formation: 1.10.4.1.2, 1.10.4.3.4
- C₁₂H₃₆ClP₃Si₄**
 {[CH(CH₃)₃Si]₂P}₂PCl
 Reaction with (CH₃)₃CLi: 1.5.4.2.4
- C₁₂H₃₆F₆IrP₅**
 [Ir(PMe₃)₄][PF₆]
 Reaction with H₂CO: 1.10.5.3
- C₁₂H₃₆FeP₄**
 HFe(CH₂PMe₂)(PMe₃)₃
 Formation: 1.10.2
- C₁₂H₃₆Ge₆P₄**
 [(CH₃)₂Ge]₆P₄
 Formation: 1.5.4.2.4
- C₁₂H₃₆Li₂Si₆**
 Li₂[(CH₃)₂Si]₆
 Hydrolysis: 1.6.3.2.1
- C₁₂H₃₆N₂Si₄Sn**
 {[CH(CH₃)₃Si]₂N}₂Sn
 Reaction with protonic acids: 1.5.3.1.3
- C₁₂H₃₆N₄Si₄**
 [(CH₃)₃Si]₄N₄
 Reaction with CF₃CO₂H: 1.5.3.1.3
- C₁₂H₃₆N₆W₂**
 W₂(NMe₂)₆
 Reaction with 2-propanol: 1.10.5.6.1
- C₁₂H₃₆P₄Pd**
 Pd(PMe₃)₄
 Reaction with HCl: 1.10.5.1
- C₁₂H₃₆P₄Si₄**
 [(CH₃)₃SiP]₄
 Methanolysis: 1.5.3.2.3
- C₁₂H₃₆Si₆**
 [(CH₃)₂Si]₆
 Photolysis in presence of HCl: 1.6.4.2.3
 Photolysis in presence of C₆H₁₀: 1.6.4.2.3
 Precursor to (CH₃)₂Si: 1.6.3.2.1, 1.6.3.2.3

- Reaction with HCl: 1.6.3.2.3
- C₁₂H₃₇ClSi₆**
H[(CH₃)₂Si]₆Cl
Formation: 1.6.3.2.3
- C₁₂H₃₈Cl₆P₄Ta₂**
H₂Ta₂Cl₆[P(CH₃)₃]₄
Formation: 1.10.4.1.3
- C₁₂H₃₈OsP₄**
H₂Os(PMe₃)₄
Equilibrium basicity at metal: 1.10.6.1.2
- C₁₂H₃₈Si₆**
H₂[(CH₃)₂Si]₆
Formation: 1.6.3.2.1
- C₁₂H₅₁B₃₀ClIrP₃**
HClIr[C₂B₁₀H₁₀P(CH₃)₂](C₂B₁₀H₁₁)*
PMe₂)₂
Formation: 1.10.5.2
- C₁₂Ir₄O₁₂**
Ir₄(CO)₁₂
Reaction with Li[Et₃BH]: 1.10.7.2
Reaction with alcoholic base: 1.10.8
- C₁₂K₄O₁₂Ru₄**
K₄[Ru₄(CO)₁₂]
Protonation on metal core: 1.10.6.2.4
- C₁₂O₁₂Os₃**
Os₃(CO)₁₂
Protonation at metal-metal bond:
1.10.6.1.4
Reaction with NH₃: 1.10.5.5.1
Reaction with H₂: 1.10.3.1, 1.10.4.3.4
Reaction with H₂ and Ni₂(C₅H₅)₂(C*
O)₂: 1.10.3.2
Reaction with H₂O: 1.10.5.6.1
Reaction with H₂S: 1.10.5.6.2
Reaction with alkoxyborohydride:
1.10.7.2
Reaction with aniline: 1.10.5.5.1
- C₁₂O₁₂Ru₃**
Ru₃(CO)₁₂
Hydrolysis: 1.10.9
Reaction with NaBH₄: 1.10.5.2
Reaction with EtSH: 1.10.5.6.2
Reaction with H₂: 1.10.3.2, 1.10.4.3.3
Reaction with H₂ and Ni₂(C₅H₅-
h⁵)₂(CO)₂: 1.10.3.2
- C₁₃CoKO₁₃Ru₃**
K[CoRu₃(CO)₁₃]
Protonation at metal core: 1.10.6.2.4
- C₁₃Co₂O₁₃Ru₂**
Ru₂Co₂(CO)₁₃
Reaction with H₂: 1.10.4.3.3
- C₁₃HCoO₁₃Ru₃**
HCoRu₃(CO)₁₃
Formation: 1.10.6.2.4
- Reaction with H₂: 1.10.4.3.3
- C₁₃HKO₁₃Ru₄**
K[HRu₄(CO)₁₃]
Formation: 1.10.6.2.4
- C₁₃H₂FeO₁₃Os₃**
H₂FeOs₃(CO)₁₃
Reaction with H₂: 1.10.4.3.4
- C₁₃H₂FeO₁₃Ru₃**
H₂FeRu₃(CO)₁₃
Equilibrium acidity and rate of forma-
tion by protonation of an anion:
1.10.6.2.4
Reaction with H₂: 1.10.3.2, 1.10.4.3.3
- C₁₃H₂Fe₅O₁₂**
HFe₅(CO)₁₂CH
Formation: 1.6.3.1.3
- C₁₃H₂O₁₃Ru₄**
H₂Ru₄(CO)₁₃
Equilibrium acidity and rate of forma-
tion by protonation of an anion:
1.10.6.2.4
Reactions with D₂: 1.10.4.3.3
- C₁₃H₃NO₁₁Os₃**
Os₃(NCMe)(CO)₁₁
Reaction with HCl: 1.10.5.1
- C₁₃H₅Co₃O₉**
Co₃(CO)₉CC(CH₃)CH₂
Reaction with H[PF₆]: 1.6.3.1.3
- C₁₃H₅Co₃O₁₀**
Co₃(CO)₉CCOC₂H₅
Reaction with (C₂H₅)₃SiH: 1.6.4.1.2
- C₁₃H₆Co₃F₆O₉P**
[Co₃(CO)₉CC(CH₃)₂][PF₆]
Formation: 1.6.3.1.3
- C₁₃H₇Co₃O₉**
Co₃(CO)₉CCH₂C₂H₅
Formation: 1.6.4.1.2
- C₁₃H₁₀AsCl**
(C₆H₅)₂CAsCl
Reaction with HCl: 1.6.3.1.3
- C₁₃H₁₀CIP**
(C₆H₅)₂CPCl
Reaction with HCl: 1.6.3.1.3
- C₁₃H₁₀N₂**
(C₆H₅)₂CN₂
Reaction with h⁵-C₅H₅Zr(H)Cl: 1.5.4.1.2
- C₁₃H₁₀O₃Rh₂**
(h⁵-C₅H₅)₂Rh₂(CO)₃
Protonation on metal-metal bond:
1.10.6.1.4
- C₁₃H₁₁AsCl₂**
(C₆H₅)₂CHAsCl₂
Formation: 1.6.3.1.3

- C₁₃H₁₁Br₄O₃Rh₂**
 [(h⁵-C₅H₅)₂Rh₂(CO)₃H][BF₄]
 Formation by protonation of a
 metal-metal bond: 1.10.6.1.4
- C₁₃H₁₁Cl₂P**
 (C₆H₅)₂CHPCl₂
 Formation: 1.6.3.1.3
- C₁₃H₁₁N**
 C₆H₅CHNC₆H₅
 Reaction with (n-C₄H₉)₃SnH: 1.6.4.1.3
 Reaction with H₂: 1.5.2.1.2
- C₁₃H₁₃O₂P**
 CH₃P(OC₆H₅)₂
 Reaction with H₂NP(C₆H₅)₂NP(C₆H₅)₂NH: 1.5.3.2.3
- C₁₃H₁₅N₃P**
 (C₆H₅NH)₂PNCH₃
 Redistribution: 1.5.4.1.3
- C₁₃H₂₁NOSn**
 (C₂H₅)₃SnN(C₆H₅)COH
 Reaction with (C₆H₅)₂SnH₂: 1.5.4.1.3
- C₁₃H₂₂N₂**
 C₆H₁₁NCNC₆H₁₁
 Reaction with (C₂H₅)₃SnH: 1.6.4.1.3
- C₁₃H₂₄Cl₂Mg₂NO₅Ti**
 TiMg₂Cl₂(NCO)(O)(C₄H₈O)₃
 Hydrolysis to NH₃ and CO: 1.5.3.1.1
- C₁₃H₂₄Cl₂Mg₂NO₅V**
 VMg₂Cl₂(NCO)(O)(C₄H₈O)₃
 Hydrolysis to NH₃: 1.5.3.1.1
- C₁₃H₂₆IrP**
 IrH₂(C₅Me₅-h⁵)PMe₃
 Reaction with cyclohexane: 1.10.5.3
- C₁₃H₂₈O₂Sn**
 (n-C₄H₉)₃SnCO₂H
 Thermolysis: 1.6.4.4.2
- C₁₃H₃₀BClF₄OP₂Pt**
 [PtCl(CO)(PEt₃)₂][BF₄]
 Hydrolysis: 1.10.9
- C₁₃H₃₀ClIrOP₂**
 Ir(CO)Cl[P(C₂H₅)₃]₂
 Enthalpy for reaction with H₂: 1.10.4.1.1
- C₁₃H₃₁ClO₂P₂Pt**
 trans-PtCl(COOH)(PEt₃)₂
 Generation of hydride: 1.10.9
- C₁₃H₃₂ClIrOP₄**
 [Ir(CO)(Me₂PCH₂CH₂PMe₂)₂]Cl
 Ethanolysis: 1.10.8
- C₁₃H₃₂GeSi**
 (C₂H₅)₂Ge(H)CH₂CH₂CH₂Si(C₂H₅)₃
 Formation: 1.6.4.3.3
- C₁₃H₃₂Ge₂**
 (C₂H₅)₂Ge(H)CH₂CH₂CH₂Ge(C₂H₅)₃
 Formation: 1.6.4.3.3
- C₁₃H₃₃N₃Sn**
 CH₃Sn[N(C₂H₅)₂]₃
 Reduction by B₂H₆ or (C₄H₉)₂AlH:
 1.6.4.4.3
- C₁₃H₃₈F₆IrOP₅**
 [IrH(CHO)(PMe₃)₄][PF₆]
 Formation: 1.10.5.3
- C₁₃H₃₉ClP₄Ru**
 RuClMe(PMe₃)₄
 Reaction with Na[OMe]: 1.10.8.1
- C₁₃H₄₆P₄Ru**
 RuHMe(PMe₃)₄
 Formation from Na[OMe]: 1.10.8.1
- C₁₃K₂O₁₃Ru₄**
 K₂[Ru₄(CO)₁₃]
 Protonation on metal core: 1.10.6.2.4
- C₁₄HFe₈NO₁₄**
 HFe₃N(CO)₁₄
 Formation by protonation of metal
 core: 1.10.6.2.4
- C₁₄H₆N₂O₁₀Os₃**
 Os₃(NCMe)₂(CO)₁₀
 Hydrolysis: 1.10.5.6.1
 Methanolysis: 1.10.5.6.1
 Reaction with EtSH: 1.10.5.6.2
 Reaction with HCl: 1.10.5.1
 Reaction with aniline: 1.10.5.5.1
- C₁₄H₈NiO₉Ru₃**
 Ru₃(μ-H)₃Ni(C₅H₅)(CO)₉
 Formation: 1.10.3.2
- C₁₄H₉BF₇N₂O₂Re**
 [h⁵-C₅H₅Re(CO)₂N₂-o-CF₃C₆H₄][BF₄]
 Reduction by NaBH₄: 1.5.5.1
- C₁₄H₁₀ClD₂Fe₂O₄P**
 {[h⁵-C₅H₅(CO)₂Fe]₂PD₂}Cl
 Formation: 1.5.7.2.2
- C₁₄H₁₀Cl₂Fe₂GeO₄**
 [h⁵-C₅H₅(CO)₂Fe]₂GeCl₂
 Reduction with NaBH₄: 1.6.5.3.1
- C₁₄H₁₀F₃N₂O₂Re**
 h⁵-C₅H₅Re(CO)₂NHN-o-CF₃C₆H₄
 Formation: 1.5.5.1
- C₁₄H₁₀Fe₂O₄**
 [h⁵-C₅H₅Fe(CO)₂]₂
 Protonation on metal-metal bond:
 1.10.6.1.4
- C₁₄H₁₀Mg**
 C₁₄H₁₀Mg
 Catalyst for reaction of H₂ with Mg:
 1.8.3.2
- C₁₄H₁₁F₆Fe₂O₄P**
 [[h⁵-C₅H₅Fe(CO)₂]₂H][PF₆]
 Formation by protonation of a metal-
 metal bond: 1.10.6.1.4

- C₁₄H₁₁NO₉Ru₃**
 HRu₃[μ₃-HCN(C₄H₉-t)](CO)₉
 Formation: 1.10.3.2, 1.10.4.3.3
- C₁₄H₁₂**
 trans-C₆H₅CHCHC₆H₅
 Formation: 1.6.3.1.3
- C₁₄H₁₂BF₄N₂O₂Re**
 [h⁵-C₅H₅Re(CO)₂N₂C₆H₄CH₃-p][BF₄]
 Reduction by NaBH₄: 1.5.5.1
- C₁₄H₁₂ClFe₂O₄P**
 [[h⁵-C₅H₅(CO)₂Fe]₂PH₂Cl]
 Exchange with D₂O: 1.5.7.2.2
- C₁₄H₁₂F₃OP**
 C₆H₅P[OCH(CF₃)C₆H₅][F₂H]
 Formation: 1.5.3.2.3
- C₁₄H₁₂Fe₂GeO₄**
 [h⁵-C₅H₅(CO)₂Fe]₂GeH₂
 Formation: 1.6.5.3.1
- C₁₄H₁₂O₃Ru₂**
 Ru₂(CO)₃(μ-CH₂)(C₅H₅)₂
 Reaction with H₂: 1.10.4.3.3
- C₁₄H₁₃N₂O₂Re**
 h⁵-C₅H₅Re(CO)₂NHN-p-CH₃C₆H₄
 Formation: 1.5.5.1
- C₁₄H₁₃O₂P**
 (C₆H₅)₂P(O)COCH₃
 Reaction with HCl: 1.5.3.2.3
- C₁₄H₁₃P**
 (C₆H₅)₂PCHCH₂
 Reaction with H₂P(CH₂)₂CN: 1.6.4.1.4
- C₁₄H₁₄ClOP**
 (m-CH₃C₆H₄)₂P(O)Cl
 Reduction by (C₆H₅)₂SiH₂ or HSiCl₃:
 1.5.4.2.2
- C₁₄H₁₄N₂O**
 C₆H₅(C₆H₅CH₂CH₂)NNO
 Reaction with H₂: 1.5.2.1.2
- C₁₄H₁₅As**
 (p-CH₃C₆H₄)₂AsH
 Formation: 1.5.3.3.3
- C₁₄H₁₅BCl₃OP**
 (C₆H₅)₂PCH₂OCH₃·BCl₃
 Hydrolysis: 1.5.3.2.3
- C₁₄H₁₅BCl₃PS**
 (C₆H₅)₂PCH₂SCH₃·BCl₃
 Hydrolysis: 1.5.3.2.3
- C₁₄H₁₅N**
 C₆H₅(C₆H₅CH₂CH₂)NH
 Formation: 1.5.2.1.2
- C₁₄H₁₅NO₄**
 CH₃(CH₃CO)C₆H₃CHC(CO₂H)NH-COCH₃
 Reaction with H₂ in presence of Rh chiral catalysts: 1.6.6.1
- C₁₄H₁₅NO₅**
 CH₃CO(CH₃O)C₆H₃CHC(CO₂H)NH-COCH₃
 Reaction with H₂ in asymmetric hydrogenation: 1.6.2.1.2
- C₁₄H₁₅O₂P**
 C₂H₅P(OC₆H₅)₂
 Reaction with H₂NP(C₆H₅)₂NP(C₆H₅)₂NH: 1.5.3.2.3
- C₁₄H₁₅P**
 (C₆H₅CH₂)₂PH
 Formation: 1.5.5.2.3
- C₁₄H₁₆Cl₂Rh₂**
 [Rh(C₇H₈Cl)]₂
 Reaction with H₂: 1.10.4.3.4
- C₁₄H₁₆NOP**
 C₆H₅(CH₃)NP(O)CH₃(C₆H₅)
 Cleavage by LiAlH₄: 1.5.5.2.3
 Reduction by LiAlH₄: 11.5.5.2.2
- C₁₄H₁₆NO₂P**
 C₆H₄O(NH)PH(C₂H₅)OC₆H₅
 Formation: 1.5.3.2.3
- C₁₄H₁₆NOPS**
 C₆H₄O(NH)PH(C₂H₅)SC₆H₅
 Formation: 1.5.3.2.3
- C₁₄H₁₆O₂Sn**
 (C₆H₅)₂Sn(OCH₃)₂
 Reduction by B₂H₆: 1.6.4.4.2
- C₁₄H₁₆P₂**
 (C₆H₅)₂PCH₂CH₂PH₂
 Formation: 1.5.5.2.2
- C₁₄H₁₇NO₄**
 CH₃(CH₃CO)C₆H₃CH₂CH(CO₂H)NH-COCH₃
 Industrial formation: 1.6.6.1
- C₁₄H₁₇NO₅**
 CH₃CO(CH₃O)C₆H₃CH₂CH(CO₂H)NH-COCH₃
 Formation of in asymmetric hydrogenation: 1.6.2.1.2
- C₁₄H₂₁Ir**
 HIr(C₈H₁₃)(h⁴-1,3-C₆H₈)
 Formation: 1.10.8.4
- C₁₄H₂₂Co₂P₂**
 (h⁵-C₅H₅CoPMe₂)₂
 Protonation at metal-metal bond:
 1.10.6.1.4
- C₁₄H₂₃Co₂F₆P₃**
 [(h⁵-C₅H₅CoPMe₂)₂H][PF₆]
 Formation by protonation of a metal-metal bond: 1.10.6.1.4
- C₁₄H₂₄P₂**
 o-C₆H₄(PEt₂)₂
 Reaction with Fe and H₂: 1.10.2

- C₁₄H₂₄Sn**
 (C₂H₅)₃SnCH₂CH₂C₆H₅
 Formation: 1.6.4.1.4
- C₁₄H₂₈PRh**
 HRhMe(C₅Me₅-h⁵)PMe₃
 Formation: 1.10.5.3
- C₁₄H₂₉OP**
 (t-C₄H₉CH)₂P(O)C₄H₉-t
 Tautomeric exchange: 1.5.3.2.3
- C₁₄H₃₀OP**
 (t-C₄H₉)CHCH(t-C₄H₉)P(O)(C₄H₉-t)H
 Formation in tautomeric exchange:
 1.5.3.2.3
- C₁₄H₃₀O₂Pb**
 (n-C₄H₉)₃PbOC(O)CH₃
 Reaction with stannanes: 1.6.4.5.2
- C₁₄H₃₀Pb**
 (n-C₄H₉)₃PbCH=CH₂
 Reaction with stannanes: 1.6.4.5.2
- C₁₄H₃₂B₂CoF₈P₃**
 [h⁵-C₅H₅Co(PMe₃)₃][BF₄]₂
 Formation by diprotonation and loss of
 H₂: 1.10.6.1.1
- C₁₄H₃₃NSn**
 (n-C₄H₉)₃SnNHC₂H₅
 Redistribution: 1.5.4.1.3
- C₁₄H₃₄P₂Pt**
 Pt(C₂H₄)[P(C₂H₅)₃]₂
 Reaction with H₂: 1.10.4.3.4
- C₁₄H₃₅ClP₂Pt**
 Pt(C₂H₅)Cl[P(C₂H₅)₃]₂
 Formation: 1.6.4.1.4
- C₁₄H₃₅N₃Sn**
 C₂H₅Sn[N(C₂H₅)₂]₃
 Reduction by B₂H₆ or (C₄H₉)₂AlH:
 1.6.4.4.3
- C₁₄H₃₆N₂Si₂Sn**
 {[(CH₃)₃Si][(CH₃)₃C]N }₂Sn
 Reaction with protonic acids: 1.5.3.1.3
- C₁₄H₃₈Si₄Sn**
 {[(CH₃)₃Si]₂CH }₂Sn
 Reaction with h⁵-C₅H₅Mo(CO)₃H:
 1.6.4.4.3
- C₁₅Co₆K₂O₁₅**
 K₂[Co₆(CO)₁₅]
 Protonation at metal core: 1.10.6.2.4
- C₁₅HCO₆KO₁₅**
 K[HC₆(CO)₁₅]
 Formation by protonation of metal
 core: 1.10.6.2.4
- C₁₅H₇NO₉Os₃**
 H₂Os₃(NHC₆H₄)(CO)₉
 Formation: 1.10.5.5.1
- H₂Os₃(NPh)(CO)₉**
 Formation: 1.10.5.5.1
- C₁₅H₉NO₁₀Ru₃**
 Ru₃(CO)₁₀[CN(C₄H₉-t)]
 Reaction with H₂: 1.10.4.3.3
- C₁₅H₁₀O₉Ru₃**
 HRu₃(CO)₉C≡CCMe₃
 Protonation on metal-metal bond:
 1.10.6.1.4
- C₁₅H₁₂O₄Rh**
 μ-CH₂[h⁵-C₅H₅Rh(CO)₂]₂
 Protonation on metal-metal bond:
 1.10.6.1.4
- C₁₅H₁₃Fe₃NO₁₁**
 [(CH₃)₄N][HFe₃(CO)₁₁]
 Reaction with C₆H₅CN: 1.5.4.1.2
 Reaction with CH₃CN: 1.5.4.1.2
- C₁₅H₁₄Fe₂O₃**
 [h⁵-C₅H₅(CO)Fe]₂(μ-CO)(μ-CH₃CH)
 Reduction by LiAlH₄: 1.6.5.1.2
- C₁₅H₁₄O₃Ru₂**
 Ru₂(CO)₃(μ-CHCH₃)(C₅H₅)₂
 Reaction with H₂: 1.10.4.3.3
- C₁₅H₁₅D₆Ni₃P₃**
 (h⁵-C₅H₅NiPD₂)₃
 Formation: 1.5.7.1.2
- C₁₅H₁₅Gd**
 (C₅H₅)₃Gd
 Reaction with HCl: 1.6.3.1.3
- C₁₅H₁₅N₂O₂Re**
 (h⁵-C₅H₅)Re(CO)₂NNCH₃(p-CH₃C₆H₄)
 Protonolysis by H[BF₄]: 1.5.3.1.1
- C₁₅H₁₅Nd**
 Nd(C₅H₅)₃
 Hydrolysis: 1.6.2.5
- C₁₅H₁₆BF₄N₂O₂Re**
 [h⁵-C₅H₅Re(CO)₂NHNHCH₃(p-CH₃C₆H₄)]BF₄
 Formation: 1.5.3.1.1
- C₁₅H₁₆Fe₃N₂O₉**
 [Fe₃(CH₃CNH)(CO)₉](CH₃)₄N
 Formation: 1.5.4.1.2
- C₁₅H₁₆MnO₂P**
 h⁵-C₅H₅Mn(CO)₂PPhMe₂
 Protonation at metal: 1.10.6.1.1
- C₁₅H₁₆O₂Ru₂**
 (h⁵-C₅H₅)₂Ru₂(CO)(CO)C(CH₃)₂
 Formation: 1.6.4.1.4
- C₁₅H₁₇AsO**
 (C₆H₅)₂AsCH₂OC₂H₅
 Conversion to (C₆H₅)₂AsH: 1.5.3.3.3
- C₁₅H₁₈NYb**
 Yb(C₅H₅)₃NH₃
 Reductive elimination of C₅H₆: 1.6.4.1.5

- C₁₅H₁₈Ta**
H₃Ta(h⁵-C₅H₅)₃
Catalyst in D₂ exchange with C₆H₆:
1.6.7.2.1
- C₁₅H₁₉O₃Re**
[h⁵-(CH₃)₆C₆H] Re(CO)₃
Formation: 1.6.5.1.4
- C₁₅H₂₁CoO₆**
Co(acac)₃
Reduction with (i-Bu)₂AlOEt: 1.10.8.2
Reduction with (i-Bu)₃Al: 1.10.8.2
- C₁₅H₂₁MoO₆**
Mo(acac)₃
Reaction with AlEt₃: 1.10.8.2
- C₁₅H₂₁Ni₃P₃**
[h⁵-(C₅H₅)NiPH₂]₃
Formation: 1.5.3.2.3
- C₁₅H₂₇O₂PSn**
(C₂H₅)₃SnCH₂P(O)(C₆H₅)OC₂H₅
Reduction with LiAlH₄: 1.6.5.4.3
- C₁₅H₃₃PPt**
h³-C₃H₅PtHP(CMe₃)₃
Formation: 1.10.9
- C₁₅H₃₇ClP₂Pt**
trans-(n-Pr)PtCl(PEt₃)₂
Formation: 1.10.8.4
- C₁₅H₄₅FeO₁₅P₅**
Fe[P(OMe)₃]₅
Protonation at metal: 1.10.6.1.1
- C₁₅H₄₆F₆FeO₁₅P₆**
[HFe[P(OMe)₃]₅][PF₆]
Formation by metal protonation:
1.10.6.1.1
- C₁₅H₄₆N₃PSi₅**
{[(CH₃)₃Si]₂N}₂P(H)NSi(CH₃)₃
Formation: 1.5.3.2.3
- C₁₆H₇NO₁₀Os₃**
Os₃H(NHPh)(CO)₁₀
Formation: 1.10.5.5.1
- C₁₆H₉NO₁₁Ru₃**
Ru₃(CO)₁₁[CN(C₄H₉-t)]
Reaction with H₂: 1.10.3.2, 1.10.4.3.3
- C₁₆H₁₀Cr₂O₆**
Cr₂(C₅H₅)₂(CO)₆
Reaction with H₂: 1.10.3.2
- C₁₆H₁₀O₆W₂**
[h⁵-C₅H₅W(CO)₃]₂
Protonation at metal-metal bond:
1.10.6.1.4
- C₁₆H₁₁F₆O₆PW₂**
[[h⁵-C₅H₅W(CO)₃]₂H][PF₆]
Formation by protonation of a metal-metal bond: 1.10.6.1.4
- C₁₆H₁₂MnNO₁₂Os₂**
[Me₄N][MnOs₂(CO)₁₂]
Protonation at metal core: 1.11.6.2.4
- C₁₆H₁₃NO₁₁Ru₄**
H₄Ru₄(CO)₁₁[CN(C₄H₉-t)]
Formation: 1.10.4.3.3
- C₁₆H₁₄O₃Ru₂**
[Ru₂(CO)₃(h⁵-C₅H₅)₂(h³-C₃H₄)]
Reaction with HBF₄: 1.6.3.1.3
- C₁₆H₁₅BF₄O₃Ru₂**
[Ru₂(CO)₃(n⁵-C₅H₅)₂C(CH₃)CH₂][BF₄]
Formation: 1.6.3.1.3
- C₁₆H₁₅IrO₂**
h⁵-C₅Me₅Ir(CO)₂
Protonation at metal: 1.10.6.1.1
- C₁₆H₂₀NP**
(C₂H₅)₂PN(C₆H₅)₂
Reaction with H₂S: 1.5.3.2.3
- C₁₆H₂₀O₂Si**
(C₆H₅)₂Si(OC₂H₅)₂
Reduction by Li[AlH₄]: 1.6.5.2.2
- C₁₆H₂₂Cl₄P₂W**
WCl₄(PMe₂Ph)₂
Reaction with Na[BH₄]: 1.10.9
- C₁₆H₂₂Ru**
Ru(C₈H₁₂)(C₈H₁₀)
Reaction with H₂: 1.10.4.3.3
- C₁₆H₂₄Cl₂Ir₂**
[Ir(C₈H₁₂Cl)₂]₂
Reaction with EtOH and PEt₂Ph: 1.10.8
Reaction with MeMgI: 1.10.8.4
Reaction with i-PrMgBr: 1.10.8.4
- C₁₆H₂₄Cl₄Ni₂**
{[(CH₃)₄C₄]NiCl₂]₂
Reduction with Zn: 1.6.2.5
- C₁₆H₂₄Pt**
Pt(C₈H₁₂)₂
Reaction with phosphines: 1.10.4.1.2
- C₁₆H₂₆Cl₄Ir₂**
[IrHCl₂(C₈H₁₂)]₂
Formation: 1.10.8
- C₁₆H₂₇Al**
(i-C₄H₉)₂AlCH₂CH₂C₆H₅
Formation: 1.6.4.1.4
- C₁₆H₂₇PPt**
Pt(C₂H₄)₂[P(C₆H₅)(C₃H₇-i)]₂
Reaction with H₂: 1.10.4.3.4
- C₁₆H₂₈O₄PSi**
CH₃(C₆H₅)CHC[OSi(CH₃)₃]*
P(O)(OC₂H₅)₂
Formation: 1.5.3.2.2

- C₁₆H₂₉P₂Re**
H₇Re[P(CH₃)₂C₆H₅]₂
Formation: 1.10.4.3.2
- C₁₆H₃₂ClIrSi**
h⁵-C₅Me₅IrH₂(SiEt₃)Cl
Formation: 1.10.5.4
- C₁₆H₃₃ClP₂Ru**
h⁵-C₅Me₅Ru(PMe₃)₂Cl
Reaction with organomagnesium halide reagents: 1.10.8.2
- C₁₆H₃₃CoP₂**
h⁵-C₅Me₅Co[P(Me)₃]₂
Protonation at metal: 1.10.6.1.1
- C₁₆H₃₄CoF₆P₃**
[h⁵-C₅Me₅Co(PMe₃)₂H][PF₆]
Formation: 1.10.6.1.1
- C₁₆H₃₄GeO₂**
(n-C₄H₉)₃GeCH₂CH₂CO₂CH₃
Formation: 1.6.4.1.4
- C₁₆H₃₄P₂Ru**
h⁵-C₅Me₅Ru(PMe₃)₂H
Formation from Me₂CHMgCl and Me₃CMgCl: 1.10.8.2
- C₁₆H₃₅PPt**
Pt(C₂H₄)₂[P(C₄H₉-t)₃]
Reaction with H₂: 1.10.4.3.4
- C₁₆H₃₆Ir₂N₆O₂P₂S₂**
{Ir(μ-SC₄H₉-t)(CO)P(NCH₃)₃}₂
Reaction with H₂: 1.10.4.1.1
- C₁₆H₃₆Ir₂O₂P₂S₂**
{Ir(μ-S-t-C₄H₉)(CO)P(CH₃)₃}₂
Reaction with H₂: 1.10.4.1.1
- C₁₆H₃₆Ir₂O₈P₂S₂**
{Ir(μ-S-t-C₄H₉)(CO)P(OCH₃)₃}₂
Reaction with H₂: 1.10.4.1.1
- C₁₆H₃₆P₂S₂**
(n-C₄H₉)₂P(S)P(S)(C₄H₉-n)₂
Hydrolysis to (n-C₄H₉)₂P(S)H: 1.5.3.2.1
- C₁₆H₃₆ZrO₄**
Zr(OCMe₃)₄
Reaction with Et₂AlH and C₈H₈: 1.10.8.2
- C₁₆H₃₈Ir₂N₆O₂P₂S₂**
{HIr(μ-SC₄H₉-t)(CO)P(NCH₃)₃}₂
Formation: 1.10.4.1.1
- C₁₆H₃₈Ir₂O₂P₂S₂**
{HIr(μ-S-t-C₄H₉)(CO)P(CH₃)₃}₂
Formation: 1.10.4.1.1
- C₁₆H₃₈Ir₂O₈P₂S₂**
{HIr(μ-S-t-C₄H₉)(CO)P(OCH₃)₃}₂
Formation: 1.10.4.1.1
- C₁₆H₃₈Sn₂**
[(n-C₄H₉)₂SnH]₂
Formation: 1.6.5.4.1
- C₁₆H₄₀N₄U**
U[N(C₂H₅)₂]₄
Reaction with C₅H₆: 1.5.3.1.3
- C₁₆H₅₃B₁₀Cl₂CuN₂**
[Et₄N]₂(Cl₂CuB₁₀H₁₃)
Formation as solvate: 1.9.5.1
- C₁₇H₅Co₃O₁₀**
Co₃(CO)₉CCOC₆H₅
Reaction with (C₂H₅)₃SiH in CF₃CO₂*
H: 1.6.4.1.2
- C₁₇H₇Co₃O₉**
Co₃(CO)₉CCH₂C₆H₅
Formation: 1.6.4.1.2
- C₁₇H₁₂NO₉Os₃**
H₂Os₃(CO)₉(CH₃NCH₂C₆H₅)
Formation: 1.5.4.1.2
- C₁₇H₁₆O₅Ru₂**
Ru₂(CO)₃(μ-CHCO₂C₂H₅)(C₅H₅)₂
Reaction with H₂: 1.10.4.3.3
- C₁₇H₂₀NP**
C₆H₅NC(t-C₄H₉)P(C₆H₅)H
Formation: 1.5.3.2.2
- C₁₇H₂₁NO₉Re₂**
[Et₄N][Re₂(CO)₉H]
Formation: 1.10.7.2
- C₁₇H₂₄Zr**
(h⁵-C₅H₅)₂Zr(H)CH₂C₆H₁₁
Reaction with H₂: 1.6.2.1.2
- C₁₇H₃₈BF₄OPPt**
[h³-C₃H₅PtP(CMe₃)₃(Me₂O)][BF₄]
Reaction with borohydride: 1.10.9
- C₁₈H₂O₁₈Os₆**
H₂Os₆(CO)₁₈
Formation by diprotonation of dianion: 1.10.6.2.4
- C₁₈H₇Fe₄NO₁₃**
[pyH][HFe₄(CO)₁₃]
Formation by protonation of metal core: 1.10.6.2.4
- C₁₈H₁₃ClNO₆PS**
(C₆H₄O₂)₂PNHSO₂C₆H₄Cl
Formation: 1.5.3.1.3
- C₁₈H₁₅As**
(C₆H₅)₃As
Protonation by strong acids: 1.5.3.3.2
Reaction with H₂ over Ni: 1.6.2.1.2
- C₁₈H₁₅BO₂**
C₆H₅B(OC₆H₅)₂
Reduction to C₆H₅BH₂: 1.7.5.1

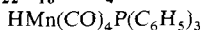
- C₁₈H₁₅BO₃**
 B(OC₆H₅)₃
 Conversion to LiBH₄ by LiAlH₄: 1.7.5.1
 Conversion to B₂H₆ by LiAlH₄: 1.7.5.1
 Reduction with H₂ and Al: 1.7.2
- C₁₈H₁₅Bi**
 (C₆H₅)₃Bi
 Reaction with H₂ over Ni: 1.6.2.1.2
- C₁₈H₁₅BiCl₂**
 (C₆H₅)₃BiCl₂
 Reduction by Li[AlH₄]: 1.5.5.5
- C₁₈H₁₅BrGe**
 (C₆H₅)₃GeBr
 Reduction by Zn in H₂O: 1.6.3.3.1
 Reduction with Li[AlH₄]: 1.6.5.3.1
- C₁₈H₁₅BrMgSi**
 (C₆H₅)₃SiMgBr
 Reaction with HCl: 1.6.3.2.3
- C₁₈H₁₅BrNP**
 (C₆H₅)₃P=NBBr
 Reduction by iodide anion: 1.5.3.1.1
- C₁₈H₁₅ClGeMg**
 (C₆H₅)₃GeMgCl
 Hydrolysis: 1.6.3.3.1
- C₁₈H₁₅ClSi**
 (C₆H₅)₃SiCl
 Reduction with LiD: 1.6.7.1.2
 Reaction with C₆H₁₁MgCl: 1.6.4.2.1
 Reduction with NaH: 1.6.4.2.1
- C₁₈H₁₅ClSn**
 (C₆H₅)₃SnCl
 Reduction by (C₂H₅)₂AlH: 1.6.4.4.1
 Reduction of Na[BH₄]: 1.6.5.4.1
 Reduction with Li[AlH₄]: 1.6.6.4
- C₁₈H₁₅DGe**
 (C₆H₅)₃GeD
 Formation: 1.6.7.1.3
- C₁₈H₁₅DSi**
 (C₆H₅)₃SiD
 Formation: 1.6.7.1.2
 Reaction with CH₂=CHCl: 1.6.7.1.1
- C₁₈H₁₅GeK**
 [(C₆H₅)₃Ge]K
 Hydrolysis: 1.6.3.3.1
- C₁₈H₁₅GeLi**
 [(C₆H₅)₃Ge]Li
 Hydrolysis: 1.6.3.3.1
 Protonation of [(C₆H₅)₃Ge]Li by [NH₄]Br in liq NH₃: 1.6.3.3.2
- C₁₈H₁₅GeNa**
 [(C₆H₅)₃Ge]Na
 Hydrolysis: 1.6.3.3.1
- C₁₈H₁₅LiPb**
 [(C₆H₅)₃Pb]Li
 Reaction with [NH₄]Br in liq NH₃: 1.6.3.5
- C₁₈H₁₅LiSn**
 (C₆H₅)₃SnLi
 Reactions with protonic acids: 1.6.3.4.1
- C₁₈H₁₅N**
 (C₆H₅)₃N
 Protonation by H₂SO₄ or hydrogen halides: 1.5.3.1.2
- C₁₈H₁₅NaSn**
 (C₆H₅)₃SnNa
 Reaction with NH₄Br in liq NH₃: 1.6.3.4.2
 Reaction with protonic acids: 1.6.3.4.1
- C₁₈H₁₅O₂P**
 C₆H₅P(OC₆H₅)₂
 Reaction with H₂NP(C₆H₅)₂NP(C₆H₅)₂NH: 1.5.3.2.3
- C₁₈H₁₅O₃P**
 (C₆H₅O)₃P
 Protonation in strong acid: 1.5.3.2.3
- C₁₈H₁₅P**
 (C₆H₅)₃P
 Formation: 1.9.2
 Protonation in strong acid: 1.5.3.2.2
 Reaction with Be(BH₄)₂: 1.8.3.1
- C₁₈H₁₅Sn**
 (C₆H₅)₃Sn
 Reaction with HCl or [NH₄][HF₂]: 1.6.3.4.3
- C₁₈H₁₆BK**
 K[HB(C₆H₅)₃]
 Formation: 1.7.4.1.3
- C₁₈H₁₆CuP**
 HCuPPh₃
 Formation: 1.10.7.2
- C₁₈H₁₆Ge**
 (C₆H₅)₃GeH
 Disproportionation at 300°C: 1.6.4.3.3
 Formation: 1.6.2.3, 1.6.3.3.1, 1.6.3.3.2, 1.6.3.3.3, 1.6.4.3.1, 1.6.4.3.3, 1.6.5.3.1, 1.6.5.3.2, 1.6.5.3.3, 1.9.2
 Industrial formation: 1.6.6.3
 Reaction with (C₂H₅)₃SnN(C₂H₅)₂: 1.5.4.1.3
 Reaction with [(C₂H₅)₂N]₃SnC₂H₅: 1.5.4.1.3
- C₁₈H₁₆GeO**
 (C₆H₅)₃GeOH
 Reduction by Li[AlH₄]: 1.6.5.3.2

- C₁₈H₁₆Mo**
 (h⁵-C₉H₇)₂MoH₂
 Formation: 1.10.2
 h⁶-C₉H₈Mo(H)C₉H₇-h⁵
 Formation: 1.10.2
- C₁₈H₁₆NP**
 (C₆H₅)₃PNH
 Reaction with Br₂: 1.5.3.1.3
 Reaction with Cl₂: 1.5.3.1.3
- C₁₈H₁₆Pb**
 (C₆H₅)₃PbH
 Formation: 1.6.3.5
- C₁₈H₁₆Si**
 (C₆H₅)₃SiH
 Formation: 1.6.2.2, 1.6.3.2.1, 1.6.3.2.3,
 1.6.4.2.1, 1.6.4.2.3
 Reaction with (C₂H₅)₃Sb: 1.6.4.1.5
 Reaction with vinyl chloride: 1.6.4.1.1
- C₁₈H₁₆Sn**
 (C₆H₅)₃SnH
 Exchange with stannyl Hg compounds:
 1.6.4.4.3
 Formation: 1.6.2.4, 1.6.3.4.1, 1.6.3.4.2,
 1.6.4.4.2, 1.6.4.4.3, 1.6.5.4.1
 Industrial formation: 1.6.6.4
 Reaction with (n-C₄H₉)₂SbCCH: 1.5.4.4
 Reaction with (C₂H₅)₃SnP(C₆H₅)₂:
 1.6.4.4.3
 Reaction with (C₂H₅)₃SnN(C₂H₅)₂:
 1.5.4.1.3
 Reaction with C₆H₅NCO: 1.6.4.1.3
- C₁₈H₁₆W**
 h⁶-C₉H₈WHC₉H₇-h⁵
 Formation: 1.10.2
- C₁₈H₁₇AsCl₂**
 [(C₆H₅)₃AsH][HCl₂]
 Formation: 1.5.3.3.2
- C₁₈H₁₇BrNP**
 [(C₆H₅)₃PNH₂][Br]
 Formation: 1.5.3.1.3
- C₁₈H₁₇ClNP**
 [(C₆H₅)₃PNH₂][Cl]
 Formation: 1.5.3.1.3
- C₁₈H₁₈AlLiSi**
 Li[H₃AlSi(C₆H₅)₃]
 Hydrolysis: 1.6.3.2.1
- C₁₈H₁₈BP**
 (C₆H₅)₃PBH₃
 From Be(BH₄)₂ and (C₆H₅)₃P: 1.8.3.1
- C₁₈H₁₈N₃P**
 (C₆H₅NH)₃P
 Formation: 1.5.3.1.3
- Redistribution: 1.5.4.1.3
- C₁₈H₁₈O₂W**
 (h⁵-C₅H₅)₂W(O₂CPh)CH₃
 Reaction with alkoxyaluminum hydrides: 1.10.7.4
- C₁₈H₁₈O₃Ru₃**
 H₃Ru₃(CO)₃(C₅H₅)₃
 Formation: 1.10.4.3.3
- C₁₈H₂₀BO₂Rh**
 [(h⁵-C₅H₅)₃Rh₃(μ-CO)₂(μ³-CH)][BH₄]
 Formation by protonation of a dinuclear methylene complex: 1.10.6.1.4
- C₁₈H₂₀LiO₂P**
 [(C₆H₄)C(CH₃)₂O]₂PLi
 Protonation to [(C₆H₄)C(CH₃)₂O]₂P⁺
 H: 1.5.3.2.3
- C₁₈H₂₀N₂O₈Ru₃**
 HRu₃[μ-HCN(t-C₄H₉)](CO)₈[CN(C₄H₉-t)]
 Formation: 1.10.4.3.3
- C₁₈H₂₁AlO**
 (C₆H₅)₂AlOC₆H₁₁
 Thermolysis: 1.6.4.1.2
- C₁₈H₂₁Cr₂NO₁₀**
 [Et₄N][HCr₂(CO)₁₀]
 Formation by protonation of a metal-metal bond: 1.10.6.2.4
- C₁₈H₂₁O₂P**
 [(C₆H₄)C(CH₃)₂O]₂PH
 Formation: 1.5.3.2.3
- C₁₈H₂₂NbP**
 (h⁵-C₅H₅)₂Nb(H)PMe₂Ph
 Formation: 1.10.9
- C₁₈H₂₃B₃CuP**
 Ph₃P · CuB₃H₈
 Formation as solvate: 1.9.5.1
- C₁₈H₂₄O₃P₂**
 (C₆H₅)₂PCH₂CH₂P(O)(OC₂H₅)₂
 Reduction by Li[AlH₄]: 1.5.5.2.2
- C₁₈H₂₅GeP**
 (C₂H₅)₃GeP(C₆H₅)₂
 Cleavage by Li[AlH₄]: 1.5.5.2.3, 1.6.5.3.3
- C₁₈H₂₅PSn**
 (C₂H₅)₃SnP(C₆H₅)₂
 Reaction with (C₆H₅)₃SnH: 1.6.4.4.3
- C₁₈H₂₆Sn₂**
 (C₂H₅)₃SnSn(C₆H₅)₂H
 Formation: 1.5.4.1.3
- C₁₈H₂₈Sn₂**
 (CH₃)₃SnSn(CH₃)₃
 Reaction with H₂: 1.6.2.4

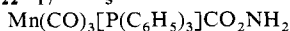
- C₁₈H₃₀N₂U**
 $\text{U}(\text{C}_5\text{H}_5)_2[\text{N}(\text{C}_2\text{H}_5)_2]_2$
 Formation: 1.5.3.1.3
- C₁₈H₃₁PPt**
 $\text{Pt}(\text{C}_2\text{H}_4)_2[\text{P}(\text{C}_6\text{H}_5)(\text{C}_4\text{H}_9\text{-}i)_2]$
 Reaction with H_2 : 1.10.4.3.4
- C₁₈H₃₃ClGeMg**
 $(\text{C}_6\text{H}_{11})_3\text{GeMgCl}$
 Hydrolysis: 1.6.3.3.1
- C₁₈H₃₃LiPb**
 $\text{Li}[(\text{C}_6\text{H}_{11})_3\text{Pb}]$
 Reaction with NH_4Br in liq NH_3 :
 1.6.3.5
- C₁₈H₃₄Ge**
 $(\text{C}_6\text{H}_{11})_3\text{GeH}$
 Formation: 1.6.3.3.1
- C₁₈H₃₄Pb**
 $(\text{C}_6\text{H}_{11})_3\text{PbH}$
 Formation: 1.6.3.5
- C₁₈H₃₅ClN₂P₂Pt**
 $\text{PtCl}(\text{N}_2\text{C}_6\text{H}_5)[\text{P}(\text{C}_2\text{H}_5)_3]_2$
 Reaction with HCl : 1.5.3.1.3
- C₁₈H₃₆ClNP₂Pt**
 $\text{PtCl}(\text{NHC}_6\text{H}_5)[\text{P}(\text{C}_2\text{H}_5)_3]_2$
 Formation: 1.5.4.1.2
- C₁₈H₃₆Cl₂N₂P₂Pt**
 $[\text{PtCl}(\text{NHNC}_6\text{H}_5)[\text{P}(\text{C}_2\text{H}_5)_3]_2]\text{Cl}$
 Formation: 1.5.3.1.3
- C₁₈H₃₆P₂Pt**
 $\text{PtH}(\text{Ph})(\text{PEt}_3)_2$
 Formation from basic MeOH : 1.10.8.1
- C₁₈H₃₉ClSi**
 $(\text{C}_6\text{H}_{13})_3\text{SiCl}$
 Reduction by LiAlH_4 : 1.6.6.2
- C₁₈H₄₀N₂Sn₂O₄**
 $[(\text{C}_2\text{H}_5)_3\text{SnN}(\text{CO}_2\text{C}_2\text{H}_5)]_2$
 Hydrolysis: 1.5.3.1.3
- C₁₈H₄₀Si**
 $(\text{C}_6\text{H}_{13})_3\text{SiH}$
 Industrial formation: 1.6.6.2
- C₁₈H₄₂HgSn₂**
 $[(n\text{-C}_3\text{H}_7)_3\text{Sn}]_2\text{Hg}$
 Exchange reaction with $(\text{C}_6\text{H}_5)_3\text{SnH}$:
 1.6.4.4.3
- C₁₈H₄₂P₂Pt**
 $\text{Pt}[\text{P}(\text{C}_3\text{H}_7\text{-}i)_3]_2$
 Hydrolysis: 1.10.5.6.1
 Reaction with SnHPh_3 : 1.10.5.4
 Reaction with H_2 : 1.10.4.1.2
- C₁₈H₄₃P₂Rh**
 $\text{HRh}[\text{P}(\text{C}_3\text{H}_7\text{-}i)_3]_2$
 Reaction with H_2 : 1.10.4.1.3
- C₁₈H₄₄OP₂Pt**
 $\text{HPt}(\text{OH})[\text{P}(\text{C}_3\text{H}_7\text{-}i)_3]_2$
 Formation: 1.10.5.6.1
- C₁₈H₄₄P₂Pt**
 $\text{H}_2\text{Pt}[\text{P}(\text{C}_3\text{H}_7\text{-}i)_3]_2$
 Formation: 1.10.4.1.2
- C₁₈H₄₅BiGe₃**
 $[(\text{C}_2\text{H}_5)_3\text{Ge}]_3\text{Bi}$
 Reaction with $(\text{CH}_3)_3\text{SnH}$: 1.6.4.3.3
- C₁₈H₄₅BiSi₃**
 $[(\text{C}_2\text{H}_5)_3\text{Si}]_3\text{Bi}$
 Reaction with $(\text{C}_2\text{H}_5)_3\text{GeH}$: 1.6.4.2.3
- C₁₈H₄₅Cl₃IrP₃**
 $\text{IrCl}_3(\text{PC}_2\text{H}_5)_3$
 Reaction with KOH and EtOH : 1.10.8
- C₁₈H₄₅Ge₃Sb**
 $[(\text{C}_2\text{H}_5)_3\text{Ge}]_3\text{Sb}$
 Reaction $(\text{CH}_3)_3\text{SnH}$: 1.6.4.3.3
- C₁₈H₄₅Ge₃Tl**
 $[(\text{C}_2\text{H}_5)_3\text{Ge}]_3\text{Tl}$
 Reaction with $(\text{C}_2\text{H}_5)_3\text{SnH}$: 1.6.4.3.3
- C₁₈H₄₅P₂Rh**
 $\text{H}_3\text{Rh}[\text{P}(\text{C}_3\text{H}_7\text{-}i)_3]_2$
 Formation: 1.10.4.1.3, 1.10.4.3.4
- C₁₈H₄₅P₃Pt**
 $\text{Pt}[\text{P}(\text{C}_2\text{H}_5)_3]_3$
 Protonation: 1.10.6.1.1
- C₁₈H₄₆Cl₂IrP₃**
 $\text{HIrCl}_2(\text{PC}_2\text{H}_5)_3$
 Formation: 1.10.8
- C₁₈H₅₄ClN₃Si₆Th**
 $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{ThCl}$
 Reaction with $t\text{-BuLi}$: 1.10.8.4
- C₁₈H₅₅N₃Si₆Th**
 $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{ThH}$
 Formation: 1.10.8.4
- C₁₈H₅₆OP₆Ru₂**
 $\text{Ru}_2(\mu\text{-OH})(\mu\text{-H})[\text{P}(\text{CH}_3)_3]_6$
 Formation: 1.10.5.6.1
- C₁₈H₅₈Mo₂P₆**
 $(\text{Me}_3\text{P})_3\text{HMo}(\mu\text{-H}_2)\text{MoH}[\text{P}(\text{CH}_3)_3]_3$
 Formation: 1.10.9
- C₁₈O₁₈Os₆**
 $\text{Os}_6(\text{CO})_{18}$
 Reaction with $\text{Na}[\text{BH}_4]$: 1.10.9
- C₁₉H₁₅ClIrOP**
 $\text{IrCl}(\text{CO})\text{PPh}_3$
 Reaction with H_2S : 1.10.5.6.2
- C₁₉H₁₅OP**
 $(\text{C}_6\text{H}_5)_2\text{PC}(\text{O})\text{C}_6\text{H}_5$
 Hydrolysis: 1.5.3.2.3

- C₁₉H₁₇AsO**
(C₆H₅)₂AsCH₂OC₆H₅
Conversion to (C₆H₅)₂AsH: 1.5.3.3.3
- C₁₉H₁₇P**
(C₆H₅)₃P=CH₂
Reaction with HCl: 1.6.3.1.3
- C₁₉H₁₈ClP**
[(C₆H₅)₃PCH₃]⁺Cl⁻
Formation: 1.6.3.1.3
- C₁₉H₁₈NP**
(C₆H₅)₃PNCH₃
Hydrolysis: 1.5.3.1.3
- C₁₉H₃₆ClNOP₂Pt**
PtCl(NHCOC₆H₅)[P(C₂H₅)₃]₂
Formation: 1.5.4.1.2
- C₁₉H₃₈N₂Sn**
C₆H₁₁NCHN[Sn(C₂H₅)₃]₂C₆H₁₁
Formation: 1.6.4.1.3
- C₁₉H₃₉Al**
n-C₇H₁₅CH[(i-C₄H₉)₂Al]CH₂CHCH₂
Formation: 1.6.4.1.4
- C₁₉H₃₉BF₄OP₂Pt**
[Pt(MeOH)Ph(PEt₃)₂][BF₄]⁻
Reaction with basic MeOH: 1.10.8.1
- C₁₉H₄₂BrIrOP₂**
Ir(CO)Br[P(i-C₃H₇)₃]₂
Enthalpy for reaction with H₂: 1.10.4.1.1
- C₁₉H₄₂ClIrOP₂**
Ir(CO)Cl[P(i-C₃H₇)₃]₂
Enthalpy for reaction with H₂: 1.10.4.1.1
- C₁₉H₄₂IrOP₂**
Ir(CO)I[P(i-C₃H₇)₃]₂
Enthalpy for reaction with H₂: 1.10.4.1.1
- C₁₉H₄₄P₂Pt**
H₂Pt[(t-C₄H₉)₂P(CH₂)₃P(C₄H₉-t)]₂
Formation: 1.4.1.2
- C₁₉H₄₅O₃P₂Rh**
RhH₂(O₂COH)[P(C₃H₇-i)]₃₂
Formation: 1.10.5.6.1
- C₂₀H₁₄N₂O₈Os₃**
Os₃H₂(NHC₆H₄)(CO)₈H₂NC₆H₅
Formation: 1.10.5.5.1
- C₂₀H₁₇Cl₂Ir₂**
h⁵-C₅Me₅Ir₂(μ-H₂)Cl₂
Reaction with HSiEt₃: 1.10.5.4
- C₂₀H₁₈ClMnO₂Si**
h⁵-CH₃C₅H₄(CO)₂HMnSiCl(C₆H₅)₂
Disproportionation: 1.6.4.2.3
- C₂₀H₁₈Fe₃N₂O₉**
[(CH₃)₄N][Fe₃(C₆H₅CNH)(CO)₉]⁺
Formation: 1.5.4.1.2
- C₂₀H₂₀ClMgN₂Ti₂**
[(h⁵-C₅H₅)₂Ti]₂N₂MgCl
Protonation with HCl: 1.5.3.1.2
- C₂₀H₂₀Fe₄N₂O₁₂**
[Et₄N][Fe₄N(CO)₁₂]⁺
Protonation at metal core: 1.10.6.2.4
- C₂₀H₂₀Fe₅N₂O₁₂**
[Et₄N][Fe₅N(CO)₁₂]⁺
Protonation at metal core: 1.10.6.2.4
- C₂₀H₂₀NP**
(C₆H₅)₃PNC₂H₅
Reaction with H₂O: 1.5.3.1.3
- C₂₀H₂₂Cl₂N₂Ti₂**
[h⁵-(C₅H₅)₂TiCl]₂N₂H₂
Reaction with HCl: 1.5.3.1.3
- C₂₀H₂₂Co₃FeO₁₄P**
HFeCo₃(CO)₁₁P[OCH(CH₃)₂]₃
Formation by protonation of metal core: 1.10.6.2.4
- C₂₀H₂₂N₂O₁₀Ru₄**
H₄Ru₄(CO)₁₀[CN(C₄H₉-t)]₂
Formation: 1.10.4.3.3
- C₂₀H₂₃N₂Ti₂**
[Ti(C₅H₅)₂]₂(NH)₂H
Formation: 1.10.5.5.1
- C₂₀H₃₀Cl₃OP₂Re**
ReOCl₃(PPhEt₂)₂
Reaction with LiAlH₄: 1.10.7.2
- C₂₀H₃₀GeSi**
(C₂H₅)₂Ge(H)CH₂CH₂CH₂Si(C₆H₅)₂*
CH₃
Formation: 1.6.4.3.3
- C₂₀H₃₀N₂Ti**
[h⁵-(CH₃)₅C₅]₂TiN₂
Reaction with NaC₁₀H₇: 1.5.3.1.3
Reaction with HCl: 1.5.3.1.3
- C₂₀H₃₀Ni**
[h⁵-(CH₃)₅C₅]₂Ni
Reaction with CF₃CO₂H: 1.6.3.1.3
- C₂₀H₃₂Zr**
[h⁵-C₅(CH₃)₅]₂ZrH₂
Formation: 1.10.4.3.1
Reaction with CO: 1.10.4.3.1
- C₂₀H₃₃F₆O₃PRh₂**
[h⁵-C₅(CH₃)₅]₂Rh₂(μ-OH)₃][PF₆]⁻
Reaction with alcohols: 1.10.8.1
- C₂₀H₃₄Ge**
(n-C₄H₉)₃GeCH=CHC₆H₅
Formation: 1.6.4.1.4
- C₂₀H₃₇P₂Re**
ReH₇[P(C₂H₅)₂C₆H₅]₂
Formation: 1.10.7.2

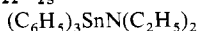
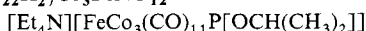
- C₂₀H₄₁ClCoN₄O₄**
 ClCo(dmgH)₂P(C₄H₉-n)₃
 Reaction with Na[BH₄]: 1.10.9
- C₂₀H₄₂CoN₄O₄**
 HCo(dmgH)₂(C₄H₉-n)₃
 Equilibrium acidity: 1.10.6.2.2
- C₂₀H₄₂CoN₄O₄P**
 HCo(dmgH)₂P(C₄H₉-n)₃
 Formation: 1.10.9
- C₂₀H₄₃F₃O₂P₂Pd**
 trans-PdH(OCOFCF₃)[P(C₃H₇-i)₃]₂
 Formation: 1.10.5.6.1
- C₂₀H₄₄P₂RuSi**
 h⁵-C₅(CH₃)₅Ru[P(CH₃)₃]₂CH₂Si(CH₃)₃
 Formation from Me₃SiCH₂MgCl:
 1.10.8.2
- C₂₀H₄₈Cl₂FeP₄**
 FeCl₂[(C₂H₅)₂PCH₂CH₂P(C₂H₅)₂]₂
 Reaction with LiAlH₄: 1.10.7.2
- C₂₀H₄₉ClRhP₄**
 HReCl(Et₂PCH₂CH₂PEt₂)₂
 Formation: 1.10.7.2
- C₂₁H₁₆CoO₃P**
 HCo(CO)₃P(C₆H₅)₃
 Equilibrium acidity: 1.10.6.2.2
- C₂₁H₁₆CoO₆P**
 HCo(CO)₃P(OC₆H₅)₃
 Equilibrium acidity: 1.10.6.2.2
- C₂₁H₁₇F₆N₄OPRu**
 [Ru(bipy)₂(CO)₄][PF₆]
 Formation from NaBH₄: 1.10.7.1
- C₂₁H₁₈BN₃**
 (C₆H₅CHN)₃B
 Formation: 1.6.4.1.3
- C₂₁H₂₀BrNiP**
 h³-C₃H₅Ni[P(C₆H₅)₃]Br
 Reaction with Na[Me₃BH]: 1.10.7.2
- C₂₁H₂₁GeK**
 K[(C₆H₅CH₂)₃Ge]
 Hydrolysis: 1.6.3.3.1
- C₂₁H₂₁GeLi**
 Li[(C₆H₅CH₂)₃Ge]
 Hydrolysis: 1.6.3.3.1
- C₂₁H₂₁GeNa**
 Na[(C₆H₅CH₂)₃Ge]
 Hydrolysis: 1.6.3.3.1
- C₂₁H₂₁O₉Os₃PS**
 HOs₃(CO)₉[P(C₂H₅)₃]SPH
 Protonation on metal-metal bond:
 1.10.6.1.4
- C₂₁H₂₂F₆O₉Os₃P₂S**
 [H₂Os₃(CO)₉[P(C₂H₅)₃]SPH][PF₆]
 Formation by protonation of a metal-metal bond: 1.10.6.1.4
- C₂₁H₂₂Ge**
 (C₆H₅CH₂)₃GeH
 Formation: 1.6.3.3.1
- C₂₁H₂₃PPtS₂**
 PtH(SCH₂CH₂SMe)P(C₆H₅)₃
 Formation: 1.10.5.6.2
- C₂₁H₂₄Si₂**
 (CH₃)₃SiSi(C₆H₅)₃
 Cleavage by Li[AlH₄]: 1.6.5.2.3
- C₂₁H₃₂OZr**
 [h⁵-C₅(CH₃)₅]₂ZrH₂CO
 Formation: 1.10.4.3.1
- C₂₁H₃₄OZr**
 [h⁵-C₅(CH₃)₅]₂ZrH(OCH₃)
 Formation: 1.10.4.3.1
- C₂₁H₄₄ClP₂Rh**
 RhCl[(t-C₄H₉)₂PCH₂CH₂CH=CHCH₂P(t-C₄H₉)₂]
 Formation: 1.10.5.3
- C₂₁H₄₆BrIrP₂**
 HIrBr[(t-C₄H₉)₂P(CH₂)₂CH(CH₂)₂P(C₄H₉-t)₂]
 Formation: 1.10.5.1
- C₂₁H₄₆ClIrP₂**
 HIrCl[(t-C₄H₉)₂P(CH₂)₂CH(CH₂)₂P(C₄H₉-t)₂]
 Reaction with H₂: 1.10.4.3.4
- C₂₁H₄₆ClP₂Rh**
 RhHCl[(t-C₄H₉)₂P(CH₂)₂CH(CH₂)₂P(t-C₄H₉)₂]
 Formation, cyclometallation: 1.10.5.3
- C₂₁H₄₉IrP₂**
 H₄Ir[(t-C₄H₉)₂P(CH₂)₂CH(CH₂)₂]^{*}
 P(C₄H₉-t)₂]
 Reaction with HBr: 1.10.5.1
- C₂₁H₄₉IrP₂**
 H₄Ir[(t-C₄H₉)₂P(CH₂)₂CH(CH₂)₂P(C₄H₉-t)₂]
 Formation: 1.10.4.3.4
- C₂₁H₆₀P₆Ru₂**
 Ru₂(μ-CH₂)₃[P(CH₃)₃]₆
 Protonation of a carbon ligand rather than a metal-metal bond: 1.10.6.1.4
- C₂₂H₁₆FeO₄Si**
 HFeSiPh₃(CO)₄
 Formation: 1.10.5.4

C₂₂H₁₆MnO₄P

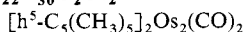
Formation: 1.10.7.2, 1.10.9

C₂₂H₁₇MnO₅PN

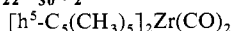
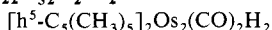
Methanolysis: 1.5.3.1.2

C₂₂H₂₅NSnReaction with $(\text{C}_6\text{H}_5)_3\text{GeH}$: 1.5.4.1.3Reaction with $(\text{C}_6\text{H}_5)_3\text{SnH}$: 1.5.4.1.3**C₂₂H₂₆BF₄OP₂Pt**Formation of hydridomethyl complex
by treatment with NaO_2CH : 1.10.9**C₂₂H₂₇Co₃FeNO₁₂P**

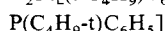
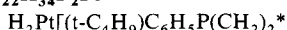
Protonation on metal core: 1.10.6.2.4

C₂₂H₃₀O₂Os₂

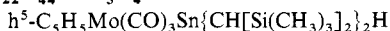
Formation: 1.10.4.3.4

C₂₂H₃₀O₂ZrReaction with H_2 : 1.10.4.3.1**C₂₂H₃₂O₂Os₂**

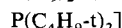
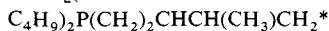
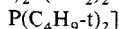
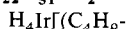
Formation: 1.10.4.3.4

C₂₂H₃₄P₂Pt

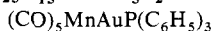
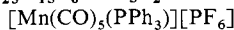
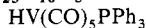
Formation: 1.10.4.1.2

C₂₂H₄₄MoO₃Si₄Sn

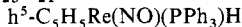
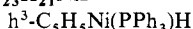
Formation: 1.6.4.4.3

C₂₂H₄₆Ni₂P₂Si₄Reaction with CH_3OD : 1.5.7.1.2**C₂₂H₄₈ClIrP₂**Reaction with H_2 : 1.10.4.3.4**C₂₂H₅₁IrP₂**

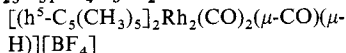
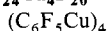
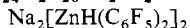
Formation: 1.10.4.3.4

C₂₃H₁₅AuMnO₅P₂Reaction with $\text{HMn}(\text{CO})_5$: 1.6.4.1.5**C₂₃H₁₅F₆MnO₅P₂**Reaction with $\text{Na}[\text{BH}_3\text{CN}]$: 1.10.7.2Reaction with $[\text{HS}]^-$: 1.10.9**C₂₃H₁₆O₅PV**

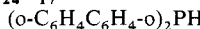
Equilibrium acidity: 1.10.6.2.2

C₂₃H₂₁NOPReFormation by decarboxylation with re-
tention at Re: 1.10.9**C₂₃H₂₁NiP**

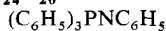
Formation: 1.10.7.2

C₂₃H₃₁BF₄O₃Rh₂Formation by protonation of a mono-
nuclear complex: 1.6.1.4**C₂₄Cu₄F₂₀**Reaction with HCl : 1.6.3.1.3**C₂₄H₂F₂₀Na₂Zn₂**

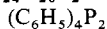
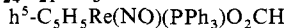
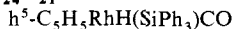
Formation: 1.9.4.2

C₂₄H₁₇P

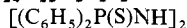
Formation: 1.5.5.2.3

C₂₄H₂₀NP

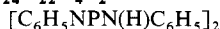
Hydrolysis: 1.5.3.1.3

C₂₄H₂₀P₂Reduction by LiAlH_4 : 1.5.5.2.3**C₂₄H₂₁NO₃PRE**Decarboxylation with retention at Re:
1.10.9**C₂₄H₂₁ORhSi**

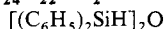
Formation: 1.10.5.4

C₂₄H₂₂N₂P₂S₂

Formation: 1.5.4.1.3

C₂₄H₂₂N₄P₂

Formation: 1.5.4.1.3

C₂₄H₂₂OSi₂Reaction with $[(\text{n-C}_4\text{H}_9)_3\text{Sn}]_2\text{O}$:
1.6.4.4.2Reduction by LiAlH_4 : 1.6.5.2.2

- C₂₄H₂₂P₄**
 (PC₆H₅)₄H₂
 Formation: 1.5.3.2.3
- C₂₄H₂₃N₃P₂**
 H₂NP(C₆H₅)₂NP(C₆H₅)₂NH
 Formation: 1.5.3.2.3
 Reaction with RP(OC₆H₅)₂: 1.5.3.2.3
- C₂₄H₂₃N₃P₂**
 H₂NP(C₆H₅)₂NP(C₆H₅)₂NH
 Reaction with C₆H₅P(OC₆H₅)₂:
 1.5.3.2.3
- C₂₄H₂₄Mo₂N₄O₄**
 Mo₂(OC₅H₉NMe)₄
 Reaction with HCl: 1.10.5.1
- C₂₄H₂₉PPtS₃**
 PtH(SCH₂CH₂SCH₂CH₂CH₂SMe)PPh₃
 Formation: 1.10.5.6.2
- C₂₄H₃₃Cl₃P₃Re**
 ReCl₃(PMe₂Ph)₃
 Reaction with Na[BH₄]: 1.10.9
- C₂₄H₃₃Cl₄P₃W**
 WCl₄(PMe₂Ph)₃
 Reaction with Na[AlH₂(OCH₂CH₂O*
 CH₃)₂]: 1.10.7.4
- C₂₄H₃₅Br₂MoN₂P₃**
 MoBr₂(NNH₂)[P(CH₃)₂C₆H₅]₃
 Formation: 1.5.3.1.2
- C₂₄H₃₅Br₂N₂P₃W**
 WBr₂(NNH₂)[P(CH₃)₂C₆H₅]₃
 Formation: 1.5.3.1.2
 Reaction with HCl: 1.5.3.1.3
- C₂₄H₃₆Br₂ClN₂P₃W**
 WClBr₂(N₂H₃)[P(CH₃)₂C₆H₅]₃
 Formation: 1.5.3.1.3
- C₂₄H₃₇BCuP₃**
 (PhMe₂P)₃CuHBH₃
 Formation: 1.9.5.1
- C₂₄H₃₈P₃Re**
 H₅Re(P(CH₃)₂C₆H₅)₃
 Formation: 1.10.9
 H₅Re[P(CH₃)₂C₆H₅]₃
 Formation and reaction with H₂:
 1.10.4.3.2
- C₂₄H₃₉P₃W**
 WH₆(PMe₂Ph)₃
 Formation: 1.10.9
- C₂₄H₄₄K₂P₄**
 K₂(C₆H₁₁P)₄
 Protonolysis to C₆H₁₁PH₂: 1.5.3.2.3
- C₂₄H₄₄Li₂P₄**
 Li₂(C₆H₁₁P)₄
 Protonolysis to C₆H₁₁PH₂: 1.5.3.2.3
- C₂₄H₅₁MoP₃**
 h⁶-C₆H₆Mo[P(C₂H₅)₃]₃
 Protonation of metal: 1.10.6.1.1
- C₂₄H₅₂F₆MoP₄**
 [h⁶-C₆H₆Mo[P(C₂H₅)₃]₃H][PF₆]
 Formation by metal protonation:
 1.10.6.1.1
- C₂₄H₅₃F₁₂MoP₅**
 [h⁶-C₆H₆Mo[P(C₂H₅)₃]₂H₂][PF₆]₂
 Formation by double metal protona-
 tion: 1.10.6.1.1
- C₂₄H₅₄HgSn₂**
 [(n-C₄H₉)₃Sn]₂Hg
 Exchange reaction with (C₆H₅)₃SnH:
 1.6.4.4.3
- C₂₄H₅₄OSn₂**
 [(n-C₄H₉)₃Sn]₂O
 Reaction with (CH₃SiHO)_x: 1.6.4.4.2,
 1.6.6.4
 Reaction with [(C₆H₅)₂SiH]₂O:
 1.6.4.4.2
- C₂₄H₅₄P₂Pd**
 Pd[P(C₄H₉)₃]₂
 Reaction with HCl: 1.10.5.1
- C₂₄H₅₄P₂Pt**
 Pt[P(C₄H₉-t)₃]₂
 Reaction with H₂: 1.10.4.1.2
- C₂₄H₅₅As₂ClPt**
 HPtCl[AsBu-t₃]₂
 Formation: 1.10.5.1
- C₂₄H₅₅Ge₂N**
 [(n-C₄H₉)₃Ge]₂NH
 Reaction with primary amines: 1.5.3.1.3
- C₂₄H₅₅N₂P₂Rh**
 HRh(N₂)[P(C₄H₉-t)₃]₂
 Reaction with H₂: 1.10.4.3.4
- C₂₄H₅₆As₂Pt**
 H₂Pt[As(C₄H₉-t)₃]₂
 Reaction with HO₂CCF₃: 1.10.5.6.1
 Reaction with HCl: 1.10.5.1
- C₂₄H₅₇P₂Rh**
 H₃Rh[P(C₄H₉-t)₃]₂
 Formation: 1.10.4.1.3, 1.10.4.3.4
- C₂₄H₆₀Cl₂O₁₂P₄Ru**
 RuCl₂[P(OC₂H₅)₃]₄
 Reaction with Na[BH₄]: 1.10.9
- C₂₄H₆₀Ge₆P₄**
 [(C₂H₅)₂Ge]₆P₄
 Formation: 1.5.4.2.4
- C₂₄H₆₀NiO₁₂P₄**
 Ni[P(OC₂H₅)₃]₄
 Equilibrium basicity at metal: 1.10.6.1.1
 Rate of protonation at metal: 1.10.6.1.3

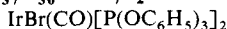
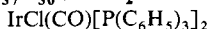
- C₂₄H₆₀O₁₂P₄Pt**
Pt[P(OC₂H₅)₃]₄
Equilibrium basicity at metal: 1.6.1.2
- C₂₄H₆₀P₄Pd**
Pd[P(C₂H₅)₃]₄
Protonation at metal: 1.10.6.1.1
- C₂₄H₆₂O₁₂P₄Ru**
H₂Ru[P(OC₂H₅)₃]₄
Formation: 1.10.9
- C₂₅H₁₆ClF₆N₄OOSp**
[Os(bipy)₂(CO)Cl][PF₆]
Reaction with PPh₃ and HOCH₂CH₂*
OH: 1.10.8.1
- C₂₅H₁₆Cl₂N₄O₈Ru**
[Ru(bipy)₂(CO)Cl][ClO₄]
Reaction with NaBH₄: 1.10.7.1
- C₂₅H₁₇F₆N₄OOSp**
[Os(bipy)₂(CO)H][PF₆]
Formation from PPh₃ and HOCH₂C*
H₂OH: 1.10.8.1
- C₂₅H₂₀ClFeO₂P**
[h⁵-C₅H₅Fe[P(C₆H₅)₃](CO)₂]₂Cl
Reaction with [OH]⁻: 1.10.9
- C₂₅H₂₀Cl₂NPPt**
[(C₆H₅)₃P]Pt(Cl)₂CNC₆H₅
Ethanolysis: 1.5.3.1.2
- C₂₅H₂₀O₂Pre**
h⁵-C₅H₅Re(CO)₂P(C₆H₅)₃
Equilibrium basicity at metal: 1.10.6.1.2
Protonation at metal: 1.10.6.1.1
- C₂₅H₂₀ReO₂P**
h⁵-C₅H₅Re(CO)₂P(C₆H₅)₃
Equilibrium basicity at metal: 1.10.6.1.2
- C₂₅H₂₁FeO₃P**
h⁵-C₅H₅FeP(C₆H₅)₃(CO)CO₂H
Formation of hydride: 1.10.9
- C₂₅H₂₁O₂ReSi**
cis-ReH[Si(C₆H₅)₃](C₅H₅-h⁵)(CO)₂
Formation: 1.10.5.4
- C₂₅H₂₂MnOP**
h⁵-MeC₅H₄Mn(CO)P(C₆H₅)₃
Reaction with alkoxyaluminum hydrides: 1.10.7.4
- C₂₅H₂₂OSn**
(C₆H₅)₃SnH(C₆H₅)CHO
Formation: 1.6.4.1.3
- C₂₅H₂₂Si**
(C₆H₅)₃SiCH₂C₆H₅
Reaction with NaH: 1.6.4.2.3*
- C₂₅H₂₃DN₃P₃**
[(C₆H₅)₂PN]₂[CH₃P(D)N]
Formation: 1.5.7.2.2
- C₂₅H₂₃MnOP**
h⁵-CH₃C₅H₄Mn(CO)P(C₆H₅)₃
Formation: 1.10.7.4
- C₂₅H₂₃MnO₂Si**
HMnSiMePh(1-C₁₀H₇)(C₅H₄CH₃-h⁵)(CO)₂
Formation: 1.10.5.4
- C₂₅H₂₄AuClN₃P₃**
[(C₆H₅)₂P]₂N₂(NH)P(CH₃)AuCl
Formation: 1.5.3.1.3
- C₂₅H₂₄N₃P₃**
[(C₆H₅)₂P]₂N₃P(CH₃)H
Reaction with (CO)AuCl: 1.5.3.1.3
Reaction with CH₃OD: 1.5.7.2.2
- C₂₅H₃₉NSn**
C₆H₅CH₂N(C₆H₅)Sn(C₄H₉-n)₃
Formation: 1.6.4.1.3
- C₂₅H₄₅FeN₅O₅**
Fe[CNO(CH₃)₃]₅
Oxidation to a dication upon diprotonation: 1.10.6.1.1
Protonation at metal: 1.10.6.1.1
- C₂₅H₄₆BF₄FeN₅**
[HFe[CNC(CH₃)₃]₅][BF₄]
Formation by metal protonation: 1.10.6.1.1
- C₂₅H₄₇B₂F₈FeN₅O**
[Fe[CNC(CH₃)₃]₅OH₂][BF₄]₂
Formation by diprotonation and loss of H₂: 1.10.6.1.1
- C₂₆H₁₈MoO₇Pre**
Re(CO)₄[(CH₃C₆H₄)₂PC₅H₄][Mo(CO)₃]
Protonation on metal-metal bond: 1.10.6.1.4
- C₂₆H₂₀NbO₃**
h⁵-C₅H₅Nb(CO)₃(C₆H₅)₃
Equilibrium basicity at metal: 1.10.6.1.1
- C₂₆H₂₀O₃V**
h⁵-C₅H₅V(CO)₃(C₆H₅)₃
Equilibrium basicity at metal: 1.10.6.1.1
- C₂₆H₂₁CrO₂P**
h⁶-C₆H₆Cr(CO)₂(C₆H₅)₃
Equilibrium basicity at metal: 1.10.6.1.2
- C₂₆H₂₂Mn₂O₄P₂**
[h⁵-C₅H₅Mn(CO)₂]₂P₂H₂(C₆H₅)₂
Formation: 1.5.3.2.3
- C₂₆H₂₄F₆P₄Rh**
[Rh[(C₆H₅)₂P]PCH₂CH₂P(C₆H₅)₂]^{*}
[PF₆]
Equilibrium basicity at metal: 1.10.6.1.1
- C₂₆H₂₆BCuO₂P₂**
[(C₆H₅)₂P]₂CuH₂BHCO₂CH₃
Formation: 1.9.5.1

- C₂₆H₂₆Cl₄MoP₂**
 MoCl₄[P(C₆H₅)₂CH₃]₂
 Reaction with Na[BH₄]: 1.10.9
- C₂₆H₂₈BCuP₂**
 [(C₆H₅)₂PCH₂]₂CuH₂BH₂
 Formation: 1.9.5.1
- C₂₆H₂₈O₁₀Os₃**
 Os₃(CO)₁₀(C₈H₁₄)₂
 Reaction with HCO₂H: 1.10.5.6.1
 Reaction with aniline: 1.10.5.5.1
- C₂₆H₂₉ClN₄O₄Rh**
 ClRh(dmgH)₂(C₆H₅)₃
 Reaction with Na[BH₄]: 1.10.9
- C₂₆H₃₀ClIrP₂**
 IrCl(PPh₃)₂
 Reaction with 1,2-C₂B₁₀H₁₂: 1.11.5.2
- C₂₆H₃₀N₄O₄PRh**
 HRh(dmgH)₂PPh₃
 Formation: 1.10.9
- C₂₆H₃₀N₄O₄Rh**
 HRh(dmgH)₂(C₆H₅)₃
 Equilibrium acidity: 1.10.6.2.2
- C₂₆H₃₃NPSi**
 (CH₃)₃SiNC₆H₅C(t-C₄H₉)P(C₆H₅)₂
 Methanolysis: 1.5.3.2.2
- C₂₆H₃₃P₂Re**
 H₇Re[P(CH₃)(C₆H₅)₂]₂
 Formation: 1.10.4.3.2
- C₂₆H₄₀Cr₂N₂O₁₀**
 [(C₂H₅)₄N]₂[Cr₂(CO)₁₀]
 Protonation on metal-metal bond:
 1.10.6.2.4
- C₂₆H₄₁FeO₂P**
 h⁵-C₅H₅[(C₆H₁₁)₃P](OC)FeC(O)CH₃
 Protonation of acyl oxygen: 1.10.6.1.1
- C₂₆H₄₂BF₄FeO₂P**
 [h⁵-C₅H₅[(C₆H₁₁)₃P](OC)Fe≡C*
 (OH)CH₃][BF₄]
 Formation by acyl protonation:
 1.10.6.1.1
- C₂₆H₅₅As₂F₃O₂Pt**
 HPt(OCOCF₃)[As(C₄H₉-t)₃]₂
 Formation: 1.10.5.6.1
- C₂₆H₆₄P₃Rh**
 HRh[P(C₃H₇-i)₃]₃
 Reaction with CO₂ and H₂O: 1.10.5.6.1
- C₂₇H₁₆F₉IrN₄O₉S₃**
 [Ir(bipy)₂(OSO₂CF₃)₂][CF₃SO₃]
 Reaction with PPh₃ and HOCH₂CH₂-
 OH: 1.10.8.1
- C₂₇H₂₄D₃IrOP₂**
 D₃Ir(CO)[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]
 Formation: 1.10.4.1.1
- C₂₇H₂₅IrOP₂**
 HIr(CO)[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]
 Reaction with D₂: 1.10.4.1.1
 Reaction with H₂: 1.10.4.1.1
- C₂₇H₂₆ClMoP**
 MoCl(h³-C₃H₅)P(C₆H₅)₃C₆H₆-h⁶
 Reaction with NaBH₄: 1.10.9
- C₂₇H₂₆ClNOPPt**
 [(C₆H₅)₃P]Pt(Cl)₂C(OC₂H₅)NHC₆H₅
 Formation: 1.5.3.1.2
- C₂₇H₂₇IrOP₂**
 H₃Ir(CO)[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂]
 Formation: 1.10.4.1.1
- C₂₇H₂₈P₂Pt**
 HPtCH₃[(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]
 Formation from methyl cation by treat-
 ment with formate ion: 1.10.9
- C₂₇H₃₇NO₁₁Ru₃**
 [(C₄H₉)₄N][HRu₃(μ-CO)(CO)₁₀]
 Protonation on bridging carbonyl oxy-
 gen: 1.10.6.2.4
- C₂₇H₃₉Br₂N₂P₃W**
 WBr₂[N₂C(CH₃)₂][P(CH₃)₂C₆H₅]₃
 Reduction by LiAlH₄: 1.5.5.1
- C₂₇H₄₄P₂Pt**
 H₂Pt[P(C₃H₇-i)₃]₃
 Formation: 1.10.4.3.4
- C₂₇H₅₈P₂PtSn**
 trans-PtH(SnPh₃)[P(C₃H₇-i)₃]
 Formation: 1.10.5.4
- C₂₇H₆₃P₃Pd**
 Pd[P(C₃H₇-i)₃]₃
 Reaction with HO₂CCF₃: 1.10.5.6.1
- C₂₇H₆₃P₃Pt**
 Pt[P(CH₃)(C₄H₉-t)₂]₃
 Formation: 1.10.4.1.2
 Pt[P(C₃H₇-i)₃]₃
 Reaction with H₂: 1.10.4.3.4
- C₂₇H₆₄P₃Rh**
 HRh{P[CH(CH₃)₂]₃]₃
 Protonation at metal: 1.10.6.1.1
 HRh[P(C₃H₇-i)₃]₃
 Reaction with H₂: 1.10.4.3.4
- C₂₈H₂₁IrNO₂P**
 Ir(C₉N₁OH₆)(CO)P(C₆H₅)₃
 Reaction with HCl: 1.10.5.1
- C₂₈H₂₂**
 C₆H₅CHC(C₆H₅)C(C₆H₅)CH(C₆H₅)
 Formation: 1.6.2.1.2, 1.6.5.1.4
- C₂₈H₂₂ClIrNO₂P**
 HIrCl(C₉NOH₆)(CO)P(C₆H₅)₃
 Formation: 1.10.5.1

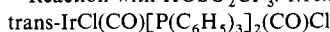
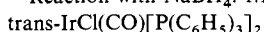
- C₂₈H₂₅ClGeTi**
 (h⁵-C₅H₅)₂TiClGe(C₆H₅)₃
 Reaction with HCl: 1.6.3.3.3
- C₂₈H₂₈MoN₄P₃**
 Mo(N₂)₂P[CH₂CH₂P(C₆H₅)₂]₂
 Reaction with HBr: 1.5.3.1.3
- C₂₈H₃₀Cl₄P₂W**
 WCl₄[P(C₆H₅)₂C₂H₅]₂
 Reaction with Li[AlH₄]: 1.10.7.2
- C₂₈H₃₂B₁₀IrO₂P**
 H₂Ir[P(C₆H₅)₃](CO)₂-7-C₆H₅-1,7-
 B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₂₈H₄₆P₂Pd**
 Pd([P(C₄H₉-t)₂C₆H₅]₂)
 Reaction with HCl: 1.10.5.1
- C₂₈H₄₆P₂Pt**
 Pt[PC₆H₅(C₄H₉-t)₂]₂
 Reaction with HO₂CCF₃: 1.10.5.6.1
 Reaction with HCl: 1.10.5.1
 Reaction with H₂: 1.10.4.1.2
- C₂₈H₄₇ClP₂Pt**
 PtHCl[(t-C₄H₉)₂PC₆H₅]₂
 Formation: 1.10.5.1
- C₂₉H₁₆NO₁₁Os₃P**
 [P(C₆H₅)₃][HOs₃(CO)₁₁]
 Formation: 1.10.7.2
- C₂₉H₃₀B₁₀IrO₃P**
 1-{Ir(CO)₃[P(C₆H₅)₃]}-7-C₆H₅-1,7-
 B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.3.4
 1-Ir[P(C₆H₅)₃](CO)₃-7-C₆H₅-1,7-
 B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
- C₂₉H₃₂B₁₀IrO₃P**
 1-{H₂Ir(CO)₃[P(C₆H₅)₃]}-7-C₆H₅-1,7-
 B₁₀C₂H₁₀
 Formation: 1.10.4.3.4
- C₂₉H₃₃B₁₀IrNOP**
 Ir[P(C₆H₅)₃](CO)(CH₃CN)-7-C₆H₅-1,7-
 B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
 Reaction with CO and H₂: 1.10.4.1.1
- C₂₉H₃₅B₁₀IrNOP**
 H₂Ir[P(C₆H₅)₃](CO)(CH₃CN)-7-C₆H₅-
 1,7-B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₂₉H₃₇B₁₀IrOP₂**
 Ir[P(CH₃)(C₆H₅)₂]₂(CO)-2-H-1,2-
 B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
- Ir[P(CH₃)(C₆H₅)₂]₂(CO)-7-H-1,7-
 B₁₀C₂H₁₀**
 Reaction with H₂: 1.10.4.1.1
- C₂₉H₃₉B₁₀IrOP₂**
 H₂Ir[P(CH₃)(C₆H₅)₂]₂(CO)-2-H-1,2-
 B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
 H₂Ir[P(CH₃)(C₆H₅)₂]₂(CO)-7-H-1,7-
 B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₃₀H₂₅PSn**
 (C₆H₅)₃SnP(C₆H₅)₂
 Hydrolysis: 1.5.3.2.3
- C₃₀H₂₅P₅**
 (C₆H₅P)₃
 Reaction with C₆H₅PH₂: 1.5.4.2.4
- C₃₀H₃₅PRu**
 (h⁶-C₆Me₆)Ru(PPh₃)₂
 Protonation at metal: 1.10.6.1.1
- C₃₀H₃₆F₆P₂Ru**
 [(h⁶-C₆Me₆)Ru(PPh₃)₃][PF₆]
 Formation by metal protonation:
 1.10.6.1.1
- C₃₀H₃₈P₄Si₂**
 (CH₃)₃Si(PC₆H₅)₄Si(CH₃)₃
 Methanolysis: 1.5.3.2.3
- C₃₀H₃₉B₁₀IrOP₂**
 Ir[P(CH₃)(C₆H₅)₂]₂(CO)-7-CH₃-1,7-
 B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
- C₃₀H₄₁B₁₀IrOP₂**
 H₂Ir[P(CH₃)(C₆H₅)₂]₂(CO)-7-CH₃-1,7-
 B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₃₀H₄₃Cl₂OsP₃**
 HOsCl₂(PBuPh)₃
 Formation: 1.10.8.2
- C₃₀H₄₅Cl₃P₃Re**
 trans-ReCl₃[P(C₂H₅)₂C₆H₅]₃
 Reaction with LiAlH₄: 1.10.7.2
- C₃₀H₄₆F₆OPRh₃**
 [[h⁵-C₅(CH₃)₅]₃Rh₃(μ-H)₃O][PF₆]
 Formation from isopropanol: 1.10.8.1
- C₃₀H₅₀P₃Re**
 ReH₅(PPhEt₂)₃
 Formation: 1.10.7.2
- C₃₁H₂₅LiOSi**
 Li[(C₆H₅)₃SiOC(C₆H₅)₂]
 Hydrolysis: 1.6.2.5
- C₃₁H₂₆OSi**
 (C₆H₅)₃SiOCH(C₆H₅)₂
 Formation: 1.6.2.5

- C₃₁H₂₈Si₂**
(C₆H₅)₃SiSi(C₆H₅)₂CH₃
Photolysis with CH₃OH: 1.6.4.2.3
- C₃₁H₃₂NP₃**
NC(CH₂)₂P[(CH₂)₂P(C₆H₅)₂]₂
Formation: 1.6.4.1.4
- C₃₁H₄₂OWZr**
(h⁵-C₅H₅)₂WC(H)OZr(H)[(CH₃)₅C₅-h⁵]₂
Formation: 1.6.4.1.2
- C₃₁H₄₆ClOP₃Ru**
HRuCl(CO)[P(C₂H₅)₂C₆H₅]₃
Formation: 1.10.8
- C₃₂H₃₀F₈O₂Pt₂**
Pt₂(μ-h¹-4,4'-MeOC₆F₄C₂C₆F₄OCH₃)(h⁴-C₈H₁₂)₂
Protonation on a metal-metal bond:
1.10.6.1.4
- C₃₂H₃₁BF₁₂O₂Pt₂**
[Pt₂(μ-H)(μ-h¹-4,4'-CH₃OC₆F₄C₂C₆*F₄OCH₃)(h⁴-C₈H₁₂)₂][BF₄]
Rearrangement to bridged vinyl complex:
1.10.6.1.4
- C₃₂H₄₄MoN₄P₄**
cis-Mo(N₂)₂[P(CH₃)₂C₆H₅]₄
Reaction with H₂SO₄: 1.5.3.1.2
Reaction with HBr: 1.5.3.1.2
Reaction with HCl: 1.5.3.1.3
- C₃₂H₄₄N₄P₄W**
cis-W(N₂)₂[P(CH₃)₂C₆H₅]₄
Reaction with H₂SO₄: 1.5.3.1.2
Reaction with HBr: 1.5.3.1.2
Reaction with HCl: 1.5.3.1.3
- C₃₂H₄₅CoP₄**
HCo[P(CH₃)₂C₆H₅]₄
Formation: 1.10.8.2
- C₃₂H₄₇P₄Re**
H₃Re[P(CH₃)₂(C₆H₅)₄]
Reaction with H₂: 1.10.4.3.2
- C₃₂H₅₆Cl₂Ir₂**
[Ir(C₈H₁₄)₂Cl]₂
Reaction with 1-(Me₂P)-1,2-C₂B₁₀H₁₁:
1.10.5.2
- C₃₃H₂₅ClMo**
h⁵-C₅H₅Mo[C₄(C₆H₅)₄-h⁴]Cl
Reaction with t-BuMgCl: 1.10.8.4
- C₃₃H₂₆Mo**
h⁵-C₅H₅Mo(C₄Ph₄-h⁴)H
Formation: 1.10.8.4
- C₃₃H₃₈ClIrOP₂**
Ir(CO)Cl[P(C₄H₉-t)(C₆H₅)₂]₂
Enthalpy for reaction with H₂: 1.10.4.1.1
- C₃₃H₄₄Ge₂P₂Pt**
[(C₂H₅)₃P]₂Pt[Ge(C₆H₅)₃][Ge(CH₃)₃]
Reaction with HCl: 1.6.3.3.3
- C₃₄H₃₀Co₂N₆O₄**
[Co(C₅H₅N)₆][Co(CO)₄]
Protonation at metal: 1.10.6.2.1
- C₃₄H₃₅B₁₀IrNOP**
Ir[P(C₆H₅)₃](CO)(C₆H₅CN)-7-C₆H₅-1,7-B₁₀C₂H₁₀
Formation: 1.10.4.1.1
Reaction with CO and H₂: 1.10.4.1.1
- C₃₄H₃₇B₁₀IrNOP**
H₂Ir[P(C₆H₅)₃](CO)(C₆H₅CN)-7-C₆H₅-1,7-B₁₀C₂H₁₀
Formation: 1.10.4.1.1
- C₃₄H₃₈F₆P₃Ir**
[h⁴-C₈H₁₂Ir[P(C₆H₅)₂CH₃]₂][PF₆]
HCl addition by initial coordination of chloride and subsequent protonation:
1.10.6.1.1
- C₃₄H₅₂P₂Pt**
H₂Pt[(C₁₀H₁₈)(C₆H₅)P(CH₂)₂P(C₁₀*H₁₈)(C₆H₅)]
Formation: 1.10.4.1.2
- C₃₅H₃₉B₁₀IrOP₂**
Ir[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂](CO)-7-C₆H₅-1,7-B₁₀C₂H₁₀
Formation and reaction with H₂:
1.10.4.1.1
- C₃₅H₄₁B₁₀IrOP₂**
H₂Ir[(C₆H₅)₂P(CH₂)₂P(C₆H₅)₂](CO)-7-C₆H₅-1,7-B₁₀C₂H₁₀
Formation: 1.10.4.1.1
Ir[P(CH₃)(C₆H₅)₂]₂(CO)-7-C₆H₅-1,7-B₁₀C₂H₁₀
Reaction with H₂: 1.10.4.1.1
- C₃₅H₄₃B₁₀IrOP₂**
H₂Ir[P(CH₃)(C₆H₅)₂]₂(CO)-7-C₆H₅-1,7-B₁₀C₂H₁₀
Formation: 1.10.4.1.1
- C₃₆H₃₀AuGeP**
(C₆H₅)₃PAuGe(C₆H₅)₃
Reaction with methanolic HCl or KCN:
1.6.3.3.3
- C₃₆H₃₀Ge₂O**
[(C₆H₅)₃Ge]₂O
Reduction by Li[AlD₄]: 1.6.7.1.3
Reduction by Li[AlH₄]: 1.6.5.3.2
- C₃₆H₃₀MgSn₂**
[(C₆H₅)₃Sn]₂Mg
Hydrolysis: 1.6.3.4.1
- C₃₆H₃₀N₂O₂OsP₂**
Os(NO)₂[P(C₆H₅)₃]₂
Reaction with HCl: 1.5.3.1.3
- C₃₆H₃₀N₆P₂Pt**
Pt(N₃)₂[P(C₆H₅)₃]₂
Reaction with HSC(O)Me: 1.10.5.6.2

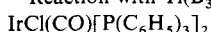
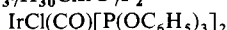
- C₃₆H₃₀Si₂**
 (C₆H₅)₃SiSi(C₆H₅)₃
 Reaction with H₂ over Cr metal: 1.6.2.2
- C₃₆H₃₀Sn₂**
 (C₆H₅)₃SnSn(C₆H₅)₃
 Reaction with H₂: 1.6.2.4
- C₃₆H₃₁AuGeP**
 (C₆H₅)₃PAuGe(C₆H₅)₃
 Formation and pyrolysis: 1.9.2
- C₃₆H₃₁ClPRhSi**
 RhHCl[Si(C₆H₅)₃]P(C₆H₅)₃
 Thermolysis: 1.6.4.2.3
- C₃₆H₃₁ClP₂Pt**
 PtClH[P(C₆H₅)₃]₂
 Reaction with (CH₃)₃SnNC(CF₃)₂:
 1.5.4.1.2
 Reaction with C₆H₅CON₃: 1.5.4.1.2
 Reaction with C₆H₅N₃: 1.5.4.1.2
- C₃₆H₃₂ClP₂IrS**
 IrH(SH)Cl[P(C₆H₅)₃]₂
 Formation: 1.10.5.6.2
- C₃₆H₃₂ClP₂RhS**
 RhH(SH)Cl[P(C₆H₅)₃]₂
 Formation: 1.10.5.6.2
- C₃₆H₃₂Cl₂N₂O₂OsP₂**
 OsCl₂(NHOH)(NO)[P(C₆H₅)₃]₂
 Formation: 1.5.3.1.3
- C₃₆H₃₂P₂PtS**
 PtH(SH)[P(C₆H₅)₃]₂
 Formation: 1.10.5.6.2
- C₃₆H₃₃Cl₃IrNOP₂**
 IrCl₃(NH₂OH)[P(C₆H₅)₃]₂
 Formation: 1.5.3.1.3
- C₃₆H₃₄BCuP₂**
 (Ph₃P)₂CuH₂BH₂
 Formation: 1.9.5.1
- C₃₆H₃₄O₂P₂Ru**
 Ru(OH)(H)[P(C₆H₅)₃]₂H₂O
 Formation: 1.10.5.6.1
- C₃₆H₃₅IrP₂**
 H₅Ir[P(C₆H₅)₃]₂
 Formation: 1.10.4.3.4
- C₃₆H₃₆BF₄IrO₂P₂**
 [H₂Ir(H₂O)₂][P(C₆H₅)₃]₂[BF₄]
 Formation: 1.10.4.3.4
- C₃₆H₃₇ClIrP₃**
 IrCl[(C₆H₅)₂P(CH₂)₃P(C₆H₅)(CH₂)₃P*
 (C₆H₅)₂]
 Reaction with H₂: 1.10.4.1.1
- C₃₆H₃₇P₂Re**
 H₇Re[P(C₆H₅)₃]₂
 Formation: 1.10.4.3.2
- C₃₆H₃₈AgB₃P₂**
 (Ph₃P)₂AgB₃H₈
 Formation as solvate: 1.9.5.1
- C₃₆H₃₈B₃CuP₂**
 (Ph₃P)₂CuB₃H₈
 Formation as solvate: 1.9.5.1
- C₃₆H₃₈B₅CuP₂**
 (Ph₃P)₂CuB₅H₈
 Formation as solvate: 1.9.5.1
- C₃₆H₃₉B₆CuP₂**
 (Ph₃P)₂CuB₆H₉
 Formation as solvate: 1.9.5.1
- C₃₆H₃₉ClIrP₃**
 H₂IrCl[(C₆H₅)₂P(CH₂)₃P(C₆H₅)*
 (CH₂)₃P(C₆H₅)₂]
 Formation: 1.10.4.1.1
- C₃₆H₆₆Cl₂NiP₂**
 NiCl₂[P(C₆H₁₁)₃]₂
 Reaction with NaBH₄: 1.10.9
- C₃₆H₆₆NiP₂**
 Ni[P(C₆H₁₁)₃]₂
 Reaction with PhOH: 1.10.5.6.1
 Reaction with pyrrole: 1.10.5.5.1
- C₃₆H₆₆P₂Pt**
 Pt[P(C₆H₁₁)₃]₂
 Formation and reaction with H₂:
 1.10.4.1.2
 Reaction with C₆HF₅: 1.10.5.3
- C₃₆H₆₇ClNiP₂**
 trans-NiHCl[P(C₆H₁₁)₃]₂
 Formation: 1.10.9
- C₃₆H₆₈P₂Pt**
 H₂Pt[P(C₆H₁₁)₃]₂
 Formation: 1.10.4.1.2
- C₃₆H₇₂P₂Ru**
 H₆Ru[P(C₆H₁₁)₃]₂
 Formation: 1.10.4.3.3
- C₃₆H₈₅CoO₁₂P₄**
 HCo{P[OCH(CH₃)₂]₃}₄
 Protonation at metal: 1.10.6.1.1
- C₃₆H₈₇P₃Pt₃**
 H₆Pt₃[P(C₄H₉-t)₃]₃
 Formation: 1.10.4.3.4
- C₃₆H₈₈P₄Ru₂**
 {H₄Ru[P(i-C₃H₇)₃]₂}₂
 Formation: 1.10.4.3.3
- C₃₆H₉₆Al₂O₈P₈Ta₂**
 {Ta[H₂Al(OCH₂CH₂OCH-
)₃]₂}[Me₂PCH₂CH₂PMe₂]₂}₂
 Formation: 1.10.7.4
- C₃₇H₃₀As₂ClIrO**
 IrCl(CO)[As(C₆H₅)₃]₂
 Equilibrium basicity at metal: 1.10.6.1.2

C₃₇H₃₀BrIrOP₂Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₃₀BrIrO₇P₂**Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₃₀ClIrOP₂**Enthalpy for reaction with H₂: 1.10.4.1.1

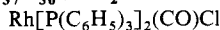
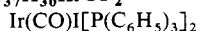
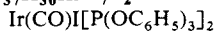
Rate of protonation at metal: 1.10.6.1.3

Reaction with HOSO₂CF₃: 1.10.5.6.1Reaction with NaBH₄: 1.10.9

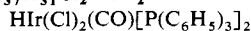
Reaction with HCl: 1.10.5.1

Reaction with Tl(B₃H₈): a:1.10.5.2Reaction with H₂: 1.10.4.1.1**C₃₇H₃₀ClIrO₇P₂**Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₃₀ClNO₂OsP₂**

Reaction with HCl: 1.5.3.1.3

C₃₇H₃₀ClOP₂RhReaction with N₂H₄: 1.10.8.2**C₃₇H₃₀IIrOP₂**Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₃₀IIrO₇P₂**Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₃₁ClIrNP₂**

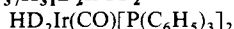
Formation: 1.10.5.3

C₃₇H₃₁Cl₂IrOP₂

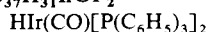
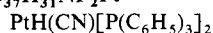
Formation: 1.10.5.1

C₃₇H₃₁Cl₂NO₂OsP₂

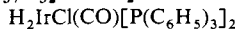
Formation: 1.5.3.1.3

C₃₇H₃₁D₂IrOP₂

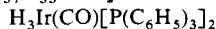
Formation: 1.10.4.3.4

C₃₇H₃₁IrOP₂Reaction with D₂: 1.10.4.3.4Reaction with H₂: 1.10.4.1.1**C₃₇H₃₁NP₂Pt**

Formation: 1.10.5.3

C₃₇H₃₂ClIrOP₂

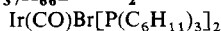
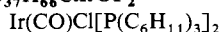
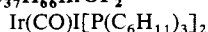
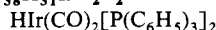
Formation: 1.10.4.1.1

C₃₇H₃₃IrOP₂

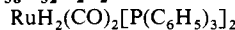
Formation: 1.10.4.1.1

C₃₇H₃₈B₃IrOP₂

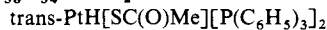
Formation: 1.10.5.2

C₃₇H₆₆BrIrOP₂Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₆₆ClIrOP₂**Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₇H₆₆IIrOP₂**Enthalpy for reaction with H₂: 1.10.4.1.1**C₃₈H₃₁IrO₂P₂**

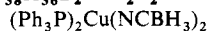
Formation: 1.10.7.2

C₃₈H₃₂O₂P₂Ru

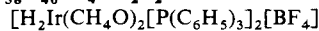
Formation: 1.10.3.2

C₃₈H₃₄OPtSP₂

Formation: 1.10.5.6.2

C₃₈H₃₆B₂CuN₂P₂

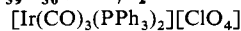
Formation: 1.9.5.1

C₃₈H₄₀BF₄IrO₂P₂

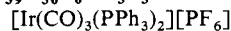
Formation: 1.10.4.3.4

C₃₈H₈₄P₄Pt₂

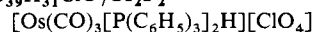
Formation: 1.10.4.1.2

C₃₉H₃₀ClIrO₇P₂

Reaction with KOH and MeOH: 1.10.8

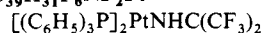
C₃₉H₃₀F₆IrO₃P₃Reaction with Li[Et₃BH]: 1.10.7.2**C₃₉H₃₀O₃OsP₂**

Protonation at metal: 1.10.6.1.1

C₃₉H₃₁ClO₇Os₂P₂

Generation by metal protonation:

1.10.6.1.1

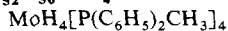
C₃₉H₃₁F₆NP₂Pt

Formation: 1.5.4.1.2

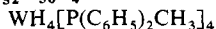
- C₃₉H₄₁B₁₀IrOP₂**
 Ir[P(C₆H₅)₃]₂CO-7-H-1,7-B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
- C₃₉H₄₁B₁₀IrOP₃**
 Ir[P(C₆H₅)₂]₃CO-2-H-1,2-B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
- C₃₉H₄₃B₁₀IrOP₂**
 H₂Ir[P(C₆H₅)₃]₂CO-2-H-1,2-B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
 H₂Ir[P(C₆H₅)₃]₂CO-7-H-1,7-B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₃₉H₄₄P₃Re**
 H₅Re[P(CH₃)(C₆H₅)₂]₃
 Formation and reaction with H₂:
 1.10.4.3.2
- C₄₀H₃₁FeNO₄P₂**
 [(Ph₃P)₂N][HFe(CO)₄]
 Formation: 1.10.9
- C₄₀H₃₃IrO₄P₂**
 Ir(CO)₂[P(C₆H₅)₃]₂CO₂CH₃
 Formation: 1.10.8
- C₄₀H₃₇OP₂Rh**
 Rh(CH₃CH₂CH₂)(CO)[P(C₆H₅)₃]₂
 Formation: 1.6.4.1.4
- C₄₀H₃₈BF₄IrN₂P₂**
 [H₂Ir(C₂H₃N)₂][P(C₆H₅)₃]₂[BF₄]
 Formation: 1.10.4.3.4
- C₄₀H₄₃B₁₀IrOP₂**
 Ir[P(C₆H₅)₃]₂(CO)-2-CH₃-1,2-B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
 Ir[P(C₆H₅)₃]₂(CO)-7-CH₃-1,7-B₁₀C₂H₁₀
 Reaction with H₂: 1.10.4.1.1
- C₄₀H₄₄BF₄IrO₂P₂**
 [H₂Ir(C₂H₆O)₂][P(C₆H₅)₃]₂[BF₄]
 Formation: 1.10.4.3.4
- C₄₀H₄₅B₁₀IrOP₂**
 H₂Ir[P(C₆H₅)₃]₂(CO)-7-CH₃-1,7-B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₄₀H₅₈FeP₂**
 H₂Fe{[o-C₆H₄(C₂H₅)₂]₂P}₂
 Formation: 1.10.2
- C₄₀H₆₀N₆Zr₂**
 {[h⁵-C₅(CH₃)₅]₂ZrN₂]₂N₂
 Reaction with H₂: 1.10.4.3.1
- C₄₀H₇₁NNiP₂**
 NiH(NC₄H₄)[P(C₆H₁₁)₃]₂
 Formation: 1.10.5.5.1
- C₄₀H₈₀P₂Pt₂Si₂**
 {PtH[μ-Si(CH₃)₂]₂P(C₆H₁₁)₃]₂
 Formation: 1.6.4.2.3
- C₄₁H₃₅ClP₂Ru**
 h⁵-C₅H₅Ru[P(C₆H₅)₃]₂Cl
 Reaction with Na[BH₄]: 1.10.9
- C₄₁H₃₆P₂Ru**
 h⁵-C₅H₅Ru[P(C₆H₅)₃]₂H
 Formation: 1.10.9
- C₄₂H₃₂F₁₂IrN₄P₃**
 [Ir(bipy)₂(PPh₃)₂H][PF₆]₂
 Formation from PPh₃ and HOCH₂C*
 H₂OH: 1.10.8.1
- C₄₂H₃₆ClNP₂Pt**
 PtCl(NHC₆H₅)[P(C₆H₅)₃]₂
 Formation: 1.5.4.1.2
- C₄₂H₃₆Co₇Fe₂O₃₀**
 [Co(Me₂CO)₆][FeCo₃(CO)₁₂]₂
 Protonation at metal core: 1.10.6.2.4
- C₄₂H₃₇O₂P₃Pt**
 PtH[P(O)(C₆H₅)₂]₂[P(OH)P(C₆H₅)₂]₂P(C₆H₅)₃
 Formation: 1.10.5.2
- C₄₂H₃₈MoP₂**
 MoH₂[P(C₆H₅)₃]₂C₆H₆-h⁶
 Formation: 1.10.9
- C₄₂H₄₃P₂Re**
 (C₆H₁₀)ReH₃[P(C₆H₅)₃]₂
 Reaction with H₂: 1.10.4.3.2
- C₄₂H₄₄BF₄IrO₂P₂**
 [H₂Ir(C₃H₆O)₂][P(C₆H₅)₃]₂[BF₄]
 Formation: 1.10.4.3.4
- C₄₂H₄₅Cl₂P₃Rh**
 RhCl₂[P(C₆H₅)₂C₂H₅]₃
 Formation: 1.10.8
- C₄₂H₄₅Ge₂NSn**
 C₂H₅Sn[Ge(C₆H₅)₃]₂N(C₂H₅)₂
 Formation: 1.5.4.1.3
- C₄₂H₄₇AgBO₂P₃**
 (Ph₂MeP)₃AgHBH₂CO₂Et
 Formation: 1.9.5.1
- C₄₂H₄₈BF₄IrO₂P₂**
 [H₂Ir(C₃H₈O)₂][P(C₆H₅)₃]₂[BF₄]
 Formation: 1.10.4.3.4
- C₄₂H₄₈P₂PtSn₂**
 Pt[Sn(CH₃)₃]₂[P(C₆H₅)₃]₂
 Reaction with H₂: 1.6.2.4
- C₄₂H₆₆BP₃Pd**
 [Pd[P(C₂H₅)₃]₃H][B(C₆H₅)₄]
 Formation by metal protonation:
 1.10.6.1.1
- C₄₂H₆₇F₅P₂Pt**
 HPt(C₆F₅)[P(C₆H₁₁)₃]₂
 Formation: 1.10.5.3

- C₄₂H₇₂Cl₃OsP₃**
 OsCl₃[P(C₄H₉-n)₂C₆H₅]₃
 Reaction with N₂H₄: 1.10.8.2
- C₄₂H₇₂NiOP₂**
 HNi(OPh)[P(C₆H₁₁)₃]₂
 Formation: 1.10.5.6.1
- C₄₃H₃₀Fe₅N₆O₁₃**
 [Fe(py)₆][Fe₄(CO)₁₃]
 Protonation at metal core: 1.10.6.2.4
- C₄₃H₃₆ClNOP₂Pt**
 PtCl(NHCOC₆H₅)[P(C₆H₅)₃]₂
 Formation: 1.5.4.1.2
- C₄₃H₃₆FeP₂**
 (h⁵-C₅H₅)Fe[(C₆H₅)₃P]₂C≡CH
 Reaction with HCl: 1.6.3.1.3
- C₄₃H₃₇ClFeP₂**
 {(h⁵-C₅H₅)Fe[(C₆H₅)₃P]₂CCH₂}Cl
 Formation: 1.6.3.1.3
- C₄₃H₃₇Cl₃NP₂Re**
 Re[P(C₆H₅)₃]₂(NC₆H₄CH₃)Cl₃
 Reaction with various basic alcohols:
 1.10.8.1
- C₄₃H₃₈Cl₂NP₂Re**
 Re(PPh₃)₂NC₆H₄CH₃(H)Cl₂
 Formation from basic isopropanol:
 1.10.8.1
- C₄₃H₃₉BNO₂P₂V**
 [(C₆H₅)₃P]₂N[h⁵-C₅H₅V(CO)₂BH₄]
 Formation: 1.10.9
- C₄₃H₄₂ClIrOP₂**
 Ir(CO)Cl[P(CH₂C₆H₅)₃]₂
 Enthalpy for reaction with H₂: 1.10.4.1.1
 Ir(CO)Cl[P(C₆H₄CH₃-p)₃]₂
 Enthalpy for reaction with H₂: 1.10.4.1.1
- C₄₄H₃₁Fe₂NO₈P₂**
 [[P(C₆H₅)₃]₂N][HFe₂(CO)₈]
 Formation by protonation of a metal-metal bond: 1.10.6.2.4
- C₄₄H₃₆As₄O₆Ru₃**
 (μ-H)₂Ru₃(CO)₆[(μ-As(C₆H₅-s)CH₂As(C₆H₅)₂)₂]
 Formation: 1.10.4.3.3
- C₄₄H₃₆NO₃V**
 [[P(C₆H₅)₃N]₂][h⁵-C₅H₅V(CO)₃H]
 Formation: 1.10.9
- C₄₄H₄₂BF₄IrP₂**
 [Ir(C₈H₁₂)[P(C₆H₅)₃]₂][BF₄]
 Reaction with H₂: 1.10.4.3.4
- C₄₄H₄₃IrP₂**
 HIr(C₈H₁₂)[P(C₆H₅)₃]₂
 Formation: 1.10.8.4
- C₄₄H₄₈BF₄IrO₂P₂**
 [H₂Ir(C₄H₈O)₂[P(C₆H₅)₃]₂][BF₄]
 Formation: 1.10.4.3.4
- C₄₄H₅₂BF₄IrO₂P₂**
 [H₂Ir(C₄H₁₀O)₂[P(C₆H₅)₃]₂][BF₄]
 Formation: 1.10.4.3.4
- C₄₅H₃₆Fe₃O₈Sb₂**
 H₃Fe₃(μ₃-COMe)(CO)₇(SbPh₃)₂
 Formation: 1.10.3.2
- C₄₅H₄₄B₁₀IrOP₂**
 Ir[P(C₆H₅)₃]₂(CO)-7-C₆H₅-1,7-B₁₀C₂H₁₀
 Reaction with RCN: 1.10.4.1.1
 Reaction with H₂: 1.10.4.1.1
- C₄₅H₄₈IrP₂**
 Ir(C₈H₁₂)[P(C₆H₅)₃]₂CH₃
 Formation: 1.10.8.4
- C₄₅H₄₇B₁₀IrOP₂**
 H₂Ir[P(C₆H₅)₃]₂(CO)-7-C₆H₅-1,7-B₁₀C₂H₁₀
 Formation: 1.10.4.1.1
- C₄₆H₄₈Ir₂O₂P₂S₂**
 {Ir(μ-SC₄H₉-t)(CO)P(C₆H₅)₃}₂
 Reaction with H₂: 1.10.4.1.1
- C₄₆H₄₉ClN₂P₂Rh**
 RhCl[P(C₆H₄CH₃-p)₃]₂C₄H₇N₂
 Reaction with H₂: 1.10.4.1.3
- C₄₆H₅₀ClP₂RhS**
 RhCl[P(p-CH₃C₆H₄)₃]₂C₄H₈S
 Reaction with H₂: 1.10.4.1.3
- C₄₆H₅₀Ir₂O₂P₂S₂**
 {Hr(μ-SC₄H₉-t)(CO)P(C₆H₅)₃}₂
 Formation: 1.10.4.1.1
- C₄₆H₅₁ClN₂P₂Rh**
 H₂RhCl[P(C₆H₄CH₃-p)₃]₂(C₄H₇N₂)
 Formation: 1.10.4.1.3
- C₄₆H₅₂ClP₂RhS**
 H₂RhCl[P(C₆H₄CH₃-p)₃]₂C₄H₈S
 Formation: 1.10.4.1.3
- C₄₇H₄₇ClNP₂Rh**
 RhCl[P(C₆H₄CH₃-p)₃]₂(C₅H₅N)
 Reaction with H₂: 1.10.4.1.3
- C₄₇H₄₉ClNP₂Rh**
 H₂RhCl[P(C₆H₄CH₃-p)₃]₂(C₅H₅N)
 Formation: 1.10.4.1.3
- C₄₈H₄₀Si₄**
 [(C₆H₅)₂Si]₄
 Reaction with Li[AlH₄]: 1.6.5.2.1,
 1.6.5.2.3
- C₄₈H₆₀GeP₂Pd**
 [(C₂H₅)₃P]₂Pd[Ge(C₆H₅)₃]₂
 Reaction with H₂: 1.6.2.3
- C₄₈H₆₀Ge₂P₂Pd**
 [(C₂H₅)₃P]₂Pd[Ge(C₆H₅)₃]₂
 Reaction with HCl: 1.6.3.3.3
- C₄₈H₆₀Ge₂P₂Pt**
 [(C₂H₅)₃P]₂Pt[Ge(C₆H₅)₃]₂
 Reaction with H₂: 1.6.2.3

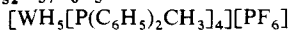
- C₄₈H₉₄P₄Pt₄**
 $\text{H}_8\text{Pt}_4[\text{P}(\text{C}_6\text{H}_5)(\text{C}_3\text{H}_7\text{-i})_2]_4$
 Formation: 1.10.4.3.4
- C₅₀H₄₀P₂Pt**
 $\text{cis-Pt}(\text{C}_6\text{H}_5\text{CCC}_6\text{H}_5)[(\text{C}_6\text{H}_5)_3\text{P}]_2$
 Reaction with HCl: 1.6.3.1.3
- C₅₀H₄₄Cl₂P₄Pt₂**
 $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pt}_2\text{Cl}_2$
 Protonation on metal-metal bond:
 1.10.6.1.4
- C₅₀H₄₅Cl₂F₆P₅Pt₂**
 $[(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Pt}_2\text{Cl}_2\text{H}][\text{PF}_6]$
 Formation by protonation of a metal-metal bond: 1.10.6.1.4
- C₅₀H₄₇P₄Pt₂**
 $\text{HPt}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2(\mu\text{-H})\text{PtH}$
 Formation: 1.10.4.3.4
- C₅₁H₄₅F₆OP₅Pt₂**
 $[\text{Pt}_2\text{H}(\text{CO})[(\mu\text{-C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2]\text{PF}_6$
 Reaction with HSMe: 1.10.5.6.2
- C₅₁H₄₅OP₄Pt₂**
 $\text{HPt}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Pt}(\text{CO})$
 Reaction with H₂: 1.10.4.3.4
- C₅₁H₄₉F₆P₄Pt₂S**
 $[\text{H}_2\text{Pt}_2(\mu\text{-SCH}_3)\mu\text{-}(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Formation: 1.10.5.6.2
- C₅₂H₄₀FeIrO₄P₃**
 $(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]\text{FeIr}[\mu\text{-P}(\text{C}_6\text{H}_5)_2](\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$
 Formation and reaction with H₂:
 1.10.4.1.3
- C₅₂H₄₄FeIrO₄P₃**
 $(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]\text{H}_2\text{FeIr}[\mu\text{-P}(\text{C}_6\text{H}_5)_2]\text{H}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]$
 Formation: 1.10.4.1.3
- C₅₂H₄₄O₂P₄Pt₂**
 $(\text{CO})\text{Pt}[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Pt}(\text{CO})$
 Reaction with H₂: 1.10.4.3.4
- C₅₂H₄₈Cl₂FeP₄**
 $\text{Fe}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Cl}_2$
 Reaction with NaBH₄: 1.10.7.1
- C₅₂H₄₈MoN₄P₄**
 trans-
 $\text{Mo}(\text{N}_2)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Reaction with H₂SO₄: 1.5.3.1.2
 Reaction with HBr: 1.5.3.1.3
 Reaction with H₂: 1.10.4.3.2
 Reaction with $[(\text{C}_2\text{H}_5\text{SFeS})_4]^{3-}$:
 1.5.3.1.3
- C₅₂H₄₈N₄P₂W**
 $\text{W}(\text{N}_2)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Reaction with HBr: 1.5.3.1.3
- C₅₂H₄₈N₄P₄W**
 $\text{W}(\text{N}_2)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Reaction with H₂SO₄: 1.5.3.1.2
- C₅₂H₄₈NiPi₄**
 $\text{Ni}[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Equilibrium basicity at metal: 1.10.6.1.1
- C₅₂H₄₉Br₂MoNP₄**
 $\{\text{MoBr}(\text{NH})[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}^*(\text{C}_6\text{H}_5)_2]_2\}\text{Br}$
 Formation: 1.5.3.1.3
- C₅₂H₄₉ClFeP₄**
 $\text{FeHCl}[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Formation: 1.10.9
- C₅₂H₅₀Br₂MoN₂P₄**
 trans-MoBr₂(N₂H₂)[(C₆H₅)₂P(CH₂)₂P*
 (C₆H₅)₂]₂
 Formation: 1.5.3.1.3
- C₅₂H₅₀Br₂N₂P₄W**
 trans-WBr₂(N₂H₂)[(C₆H₅)₂P(CH₂)₂P*
 (C₆H₅)₂]₂
 Formation: 1.5.3.1.3
- C₅₂H₅₀FeP₄**
 $\text{H}_2\text{Fe}[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Formation from NaBH₄: 1.10.7.1
- C₅₂H₅₀P₄Ru**
 $\text{H}_2\text{Ru}[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Formation: 1.10.4.3.3
- C₅₂H₅₁BrN₂P₄W**
 trans-WBr(N₂CH₃)[(C₆H₅)₂P(CH₂)₂P*
 (C₆H₅)₂]₂
 Reaction with HCl: 1.5.3.1.3
- C₅₂H₅₁MoN₂O₄P₄S**
 $\text{Mo}(\text{NNH}_2)[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2^*$
 $[\text{HSO}_4]$
 Formation: 1.5.3.1.2
- C₅₂H₅₂MoN₄P₄**
 $\text{Mo}(\text{N}_2)_2[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_4$
 Reaction with H₂SO₄: 1.5.3.1.2
- C₅₂H₅₂MoP₄**
 $\text{H}_4\text{Mo}[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
 Formation: 1.10.4.3.2
- C₅₂H₅₂N₄P₄W**
 $\text{W}(\text{N}_2)_2[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_4$
 Reaction with H₂SO₄: 1.5.3.1.2
- C₅₂H₅₂P₄Pd**
 $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3]_4$
 Reaction with HCl: 1.10.5.1
- C₅₂H₅₄P₄Ru**
 $\text{H}_2\text{Ru}[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_4$
 Formation: 1.10.4.2.1
- C₅₂H₅₅P₄Re**
 $\text{H}_3\text{Re}[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_4$
 Reaction with H₂: 1.10.4.3.2

C₅₂H₅₆MoP₄

Formation: 1.10.9

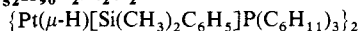
C₅₂H₅₆P₄WFormation from LiEt₃BH: 1.10.7.2

Protonation at metal: 1.10.6.1.1

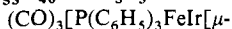
C₅₂H₅₇F₆P₅W

Formation by metal protonation:

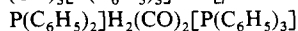
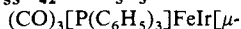
1.10.6.1.1

C₅₂H₉₀P₂Pt₂Si₂

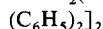
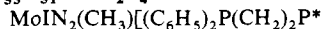
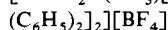
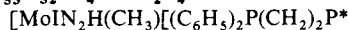
Thermolysis: 1.6.4.2.3

C₅₃H₄₀FeIrO₅P₃Formation and reaction with H₂:

1.10.4.1.3

C₅₃H₄₂FeIrO₅P₃

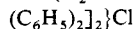
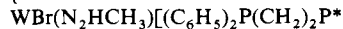
Formation: 1.10.4.1.3

C₅₃H₅₁IMoN₂P₄Protonolysis by HBF₄: 1.5.3.1.1**C₅₃H₅₂BF₄IMoN₂P₄**

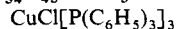
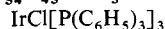
Formation: 1.5.3.1.1

C₅₃H₅₂BrClN₂P₄W

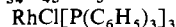
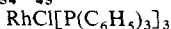
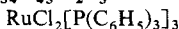
{trans-



Formation: 1.5.3.1.3

C₅₄H₃₁NO₁₈P₂Ru₆Formation by protonation of metal
core: 1.10.6.2.4**C₅₄H₄₅ClCuP₃**Reaction with LiAlH₄: 1.10.7.2**C₅₄H₄₅ClIrP₃**

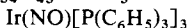
Cyclometallation: 1.10.5.3

C₅₄H₄₅ClP₃RhCatalysis of CO reaction with H₂:
1.6.6.1Reaction with H₂: 1.10.4.1.3Reaction with H₂S: 1.10.5.6.2**C₅₄H₄₅ClRh**Reduction with (i-C₃H₇)₃Al: 1.10.8.2**C₅₄H₄₅Cl₂P₃Ru**

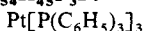
Reaction with methanolic base: 1.10.8

C₅₄H₄₅Ge₄Li

Hydrolysis: 1.6.3.3.3

C₅₄H₄₅IrNOP₃

Reaction with HCl: 1.5.3.1.3

C₅₄H₄₅P₃Pt

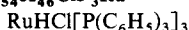
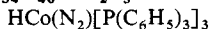
Protonation at metal: 1.10.6.1.1

Reaction with OPHPh₂: 1.10.5.2Reaction with HS(CH₂)₂SMe: 1.10.5.6.2Reaction with HS(CH₂)₂S(CH₂)₃SMe:

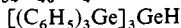
1.10.5.6.2

Reaction with H₂S: 1.10.5.6.2

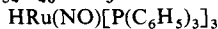
Reaction with HCN: 1.10.5.3

C₅₄H₄₆ClP₃RuReaction with AlEt₃: 1.10.8.2**C₅₄H₄₆CoN₂P₃**

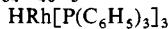
Formation: 1.10.8.2

C₅₄H₄₆Ge₄

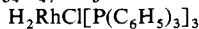
Formation: 1.6.3.3.3

C₅₄H₄₆NOP₃Ru

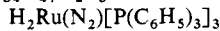
Formation: 1.10.8

C₅₄H₄₆P₃Rh

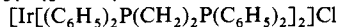
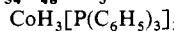
Formation: 1.10.8.2

C₅₄H₄₇ClP₃Rh

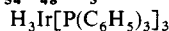
Formation: 1.10.4.1.3

C₅₄H₄₇N₂P₃Ru

Formation: 1.10.8.2

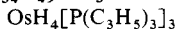
C₅₄H₄₈ClIrP₄Reaction with B₁₀H₁₄: 1.10.5.1**C₅₄H₄₈CoP₃**

Formation: 1.10.9

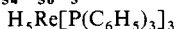
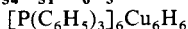
C₅₄H₄₈IrP₃

Formation: 1.10.9

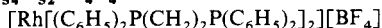
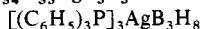
Reaction with H₂: 1.10.4.3.4

C₅₄H₄₉OsP₃

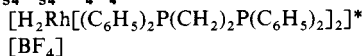
Formation: 1.10.9

C₅₄H₅₀P₃ReFormation and reaction with H₂:
1.10.4.3.2**C₅₄H₅₁Cu₆P₃**

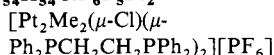
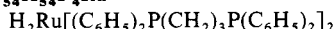
Formation as solvate: 1.9.5.1

C₅₄H₅₂BF₄P₄RhReaction with H₂: 1.10.4.2.1**C₅₄H₅₃AgB₃P₃**

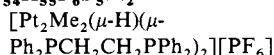
Formation as solvate: 1.9.5.1

C₅₄H₅₄BF₄P₄Rh

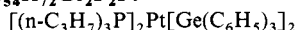
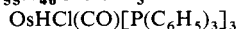
Formation: 1.10.4.2.1

C₅₄H₅₄ClF₆P₅Pt₂Reaction with NaBH₄: 1.10.9**C₅₄H₅₄P₄Ru**

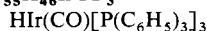
Formation: 1.10.4.2.1

C₅₄H₅₅F₆P₅Pt₂

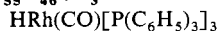
Formation: 1.10.9

C₅₄H₇₂Ge₂P₂PtReaction with LiAlH₄: 1.6.5.3.3**C₅₅H₄₆ClOOSp₃**

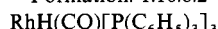
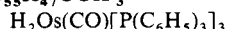
Formation: 1.10.8

C₅₅H₄₆IrOP₃

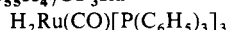
Formation: 1.10.8, 1.10.9

Loss of P(C₆H₅)₃: 1.10.4.3.4**C₅₅H₄₆OP₃Rh**

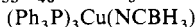
Formation: 1.10.8.2

Reaction with CH₃CH=CH₂: 1.6.4.1.4**C₅₅H₄₇OOsP₃**

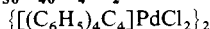
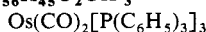
Formation: 1.10.8

C₅₅H₄₇OP₃Ru

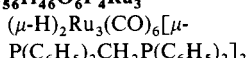
Formation: 1.10.8

C₅₅H₄₈BCuNP₃

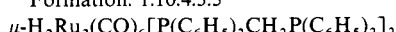
Formation as solvate: 1.9.5.1

C₅₆H₄₀Br₄Ni₂Reduction with LiAlH₄: 1.6.5.1.4**C₅₆H₄₀Cl₄Pd₂**Reaction with H₂: 1.6.2.1.2**C₅₆H₄₅O₂OsP₃**

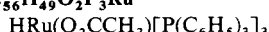
Formation: 1.10.8

C₅₆H₄₆O₆P₄Ru₃

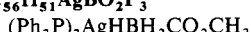
Formation: 1.10.4.3.3



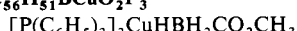
Formation: 1.10.3.2

C₅₆H₄₉O₂P₃Ru

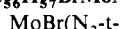
Formation: 1.10.8

C₅₆H₅₁AgBO₂P₃

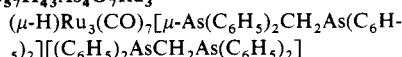
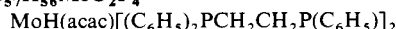
Formation: 1.9.5.1

C₅₆H₅₁BCuO₂P₃

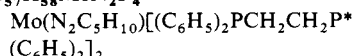
Formation: 1.9.5.1

C₅₆H₅₇BrMoN₂P₄Reduction by NaBH₄: 1.5.5.1**C₅₆H₅₈P₄Ru**

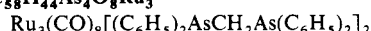
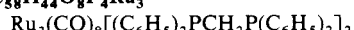
Formation: 1.10.4.2.1

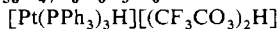
C₅₇H₄₃As₄O₇Ru₃Reaction with H₂: 1.10.4.3.3**C₅₇H₅₆MoO₂P₄**

Formation: 1.10.8.2

C₅₇H₅₈MoN₂P₄

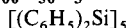
Reaction with HBr: 1.5.3.1.3

C₅₈H₄₄As₄O₈Ru₃Reaction with H₂: 1.10.4.3.3**C₅₈H₄₄O₈P₄Ru₃**Reaction with H₂: 1.10.3.2, 1.10.4.3.3

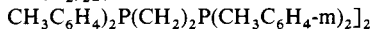
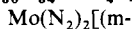
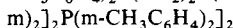
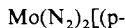
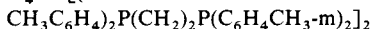
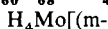
C₅₈H₄₇F₆O₆P₃Pt₆

Formation by metal protonation:

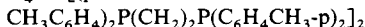
1.10.6.1.1

C₆₀H₅₀Si₅

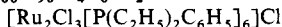
Formation: 1.6.5.2.1

C₆₀H₆₄MoN₄P₄Reaction with H₂: 1.10.4.3.2Reaction with H₂: 1.10.4.3.2**C₆₀H₆₈MoP₄**

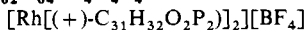
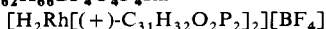
Formation: 1.10.4.3.2



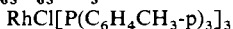
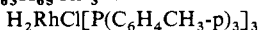
Formation: 1.10.4.3.2

C₆₀H₉₀Cl₄P₆Ru₂

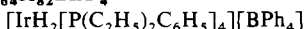
Reaction with ethanolic KOH: 1.10.8

C₆₂H₆₄BF₄O₄P₄RhReaction with H₂: 1.10.4.2.1**C₆₂H₆₄BF₄O₄P₄Rh**

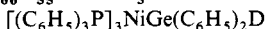
Formation: 1.10.4.2.1

C₆₃H₆₃CIP₃RhReaction with H₂: 1.10.4.1.3**C₆₃H₆₄CIP₃Rh**

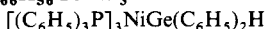
Formation: 1.10.4.1.3

C₆₄H₈₂BIrP₄

Formation: 1.11.0.8

C₆₆H₅₄DGeNiP₃

Formation: 1.6.7.2.3

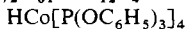
C₆₆H₅₆GeNiP₃Exchange with D₂O: 1.6.7.2.3**C₇₂H₆₀P₄Pt**

Reaction with HCN: 1.10.5.3

Reaction with phthalimide: 1.10.5.5.1

Reaction with saccharin: 1.10.5.5.1

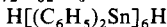
Reaction with succinimide: 1.10.5.5.1

C₇₂H₆₁CoO₁₂P₄

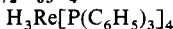
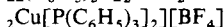
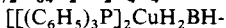
Formation: 1.10.9

C₇₂H₆₁P₄Rh

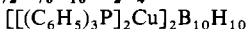
Formation: 1.10.8, 1.10.9

C₇₂H₆₂Sn₆

Formation: 1.6.3.4.3

C₇₂H₆₃P₄ReReaction with H₂: 1.10.4.3.2**C₇₂H₆₄B₂Cu₂F₄P₄**

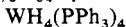
Formation: 1.9.5.1

C₇₂H₇₀B₁₀Cu₂P₄

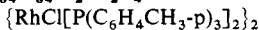
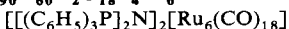
Formation: 1.9.5.1

C₇₅H₆₈P₆Ru₃

Formation: 1.10.4.3.3

C₇₆H₆₄P₄W

Formation: 1.10.7.2

C₈₄H₈₄Cl₂Rh₂P₄Reaction with H₂: 1.10.4.1.3**C₉₀H₆₀N₂O₁₈P₄Ru₆**

Protonation on metal core: 1.10.6.2.4

CaReaction with H₂: 1.8.3, 1.8.3.3**Ca*Ag₂****Ca*Al₂****CaCu₅**

Structure type: 1.12.8.1.1

CaF₂

Structure type: 1.12.5

CaGe

Protonolysis: 1.5.3.2.1, 1.6.3.3.1

CaH*Ag₂**CaH₂**

Formation: 1.8.3.3

Reaction with C₆H₅NO₂ in presence ofPtCl₂ catalyst: 1.5.4.1.1

Reaction with CO: 1.6.4.1.2

- Reaction with CO_2 : 1.6.4.1.2
 Reaction with $\text{Na}[\text{HCO}_3]$: 1.6.4.1.2
 Reduction of $(\text{CH}_3)_3\text{SiCl}$: 1.6.6.2
 CaH_4N_2
 $\text{Ca}(\text{NH}_2)_2$
 Hydrolysis to NH_3 : 1.5.3.1.1, 1.5.3.1.3
 Reaction with H_2 : 1.12.8.1.1
 $\text{CaH}_8\text{*B}_2$
 $\text{CaN}_2\text{*C}$
 $\text{CaN}_2\text{*C}_2$
 CaSi
 Hydrolysis: 1.6.3.2.3
 CaSi_2
 Hydrolysis: 1.6.3.2.1
 CaSn
 Reaction with NH_4I in liq NH_3 :
 1.6.3.4.2
 Ca_3N_2
 Hydrolysis to NH_3 : 1.5.3.1.1
 Ca_3P_2
 Reaction with D_2O : 1.5.7.1.2
 $\text{Ca}_4\text{Ge*As}_2$
 $\text{Ca}_6\text{P}_2\text{*As}_2$
 $\text{Cd*C}_2\text{H}_6$
 $\text{CdGe}_2\text{*C}_{12}\text{H}_{30}$
 CdH*Br
 CdH_2
 $(\text{CdH}_2)_n$
 Formation: 1.9.5.2
 CdH_4N_2
 $\text{Cd}(\text{NH}_2)_2$
 Hydrolysis to NH_3 : 1.5.3.1.1, 1.5.3.1.3
 $\text{CdH}_8\text{*B}_2$
 $\text{CdH}_{16}\text{Li}_2\text{*B}_4$
 $\text{CdH}_{18}\text{*B}_{12}$
 CeCo_2
 Reaction with H_2 : 1.12.8.1.2
 CeFe_2
 Reaction with H_2 : 1.12.8.1.2
 CeFe_5
 Reaction with H_2 : 1.12.8.1.1
 CeH_2
 Formation: 1.12.4.1
 CeMg_2
 Reaction with H_2 : 1.12.8.1.2
 CeNi_2
 Reaction with H_2 : 1.12.8.1.2
 CeNi_5
 Reaction with H_2 : 1.12.8.1.1
 CeRu_2
 Reaction with H_2 : 1.12.8.1.2
 Cl*CH_3
 $\text{Cl*CH}_4\text{As}$
 $\text{Cl*C}_2\text{H}_3$
 $\text{Cl*C}_2\text{H}_6\text{Bi}$
 $\text{Cl*C}_5\text{H}_{13}$
 $\text{Cl*C}_7\text{H}_7$
 $\text{Cl*C}_8\text{H}_5$
 $\text{Cl*C}_8\text{H}_7$
 $\text{Cl*C}_{12}\text{H}_{10}\text{Bi}$
 $\text{Cl*C}_{13}\text{H}_{10}\text{As}$
 $\text{ClCoN}_4\text{O}_4\text{*C}_{20}\text{H}_{41}$
 ClCs
 CsCl
 Structure type: 1.12.8.1.3
 $\text{ClCuP}_3\text{*C}_{54}\text{H}_{45}$
 ClD
 DCI
 Addition to alkenes: 1.6.7.1.1
 Cleavage of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$:
 1.6.7.1.1
 Exchange with SiH_4 : 1.6.7.2.2
 Reaction with Mg_2Ge : 1.6.7.1.3
 Reaction with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$: 1.5.7.1.1
 Reaction with $n\text{-C}_4\text{H}_9\text{MgBr}$: 1.6.7.1.1
 Reaction with $[\text{C}_{10}\text{H}_7]\text{Na}$: 1.6.7.1.1
 Reaction with amides: 1.5.7.1.1
 Reaction with germanides: 1.6.7.1.3
 $\text{ClD*C}_3\text{H}_6$
 $\text{ClD}_2\text{Fe}_2\text{O}_4\text{P*C}_{14}\text{H}_{10}$
 ClF_2P
 PF_2Cl
 Protonation in acid: 1.5.3.2.2, 1.5.3.2.3
 Reaction with NH_3 : 1.5.3.2.3
 $\text{ClF}_4\text{OP}_2\text{Pt*C}_{13}\text{H}_{30}\text{B}$
 $\text{ClF}_6\text{N}_4\text{OOSp*C}_{25}\text{H}_{16}$
 $\text{ClF}_6\text{P}_5\text{Pt}_2\text{*C}_{54}\text{H}_{54}$
 $\text{ClFeO}_2\text{*C}_{10}\text{H}_{11}$
 $\text{ClFeO}_2\text{P*C}_{25}\text{H}_{20}$
 $\text{ClFeO}_3\text{*C}_7\text{H}_7$
 $\text{ClFeO}_4\text{*C}_8\text{H}_7$
 $\text{ClFeP}_2\text{*C}_{43}\text{H}_{37}$
 $\text{ClFeP}_4\text{*C}_{52}\text{H}_{49}$
 $\text{ClFe}_2\text{O}_4\text{P*C}_{14}\text{H}_{12}$
 $\text{ClGe*C}_2\text{H}_7$
 $\text{ClGe*C}_3\text{H}_9$
 $\text{ClGe*C}_4\text{H}_{11}$
 $\text{ClGe*C}_6\text{H}_{15}$
 $\text{ClGe*C}_{12}\text{H}_{11}$
 ClGeH_3
 GeH_3Cl
 Reduction by $\text{Li}[\text{AlH}_4]$: 1.6.5.3.1
 $\text{ClGeMg*C}_6\text{H}_{15}$
 $\text{ClGeMg*C}_9\text{H}_{21}$

ClGeMg* $C_{18}H_{15}$

ClGeMg* $C_{18}H_{33}$

ClGeP* C_9H_{22}

ClGeTi* $C_{28}H_{25}$

ClH

HCl

Reaction with $(C_6H_5)_3As$: 1.5.3.3.2

Reaction with $(C_6H_5)_3PAuGe(C_6H_5)_3$:
1.6.3.3.3

Reaction with $(CH_2CH)_3B$: 1.6.3.1.3

Reaction with $(C_6F_5Cu)_4$: 1.6.3.1.3

Reaction with $(h^5-C_5H_5)Fe[(C_6H_5)_3^*P]_2CCH$: 1.6.3.1.3

Reaction with $h^4-C_4H_6Fe(CO)_3$:
1.6.3.1.3

Reaction with $(h^2-C_4H_6)Fe(CO)_4$:
1.6.3.1.3

Reaction with $h^5-C_5H_5Fe(CO)_2(CH_2C^*H=CH_2)$: 1.6.3.1.3

Reaction with $[HFe_5(CO)_{14}C]^-$:
1.6.3.1.3

Reaction with $(C_5H_5)_3Gd$: 1.6.3.1.3

Reaction with Ge metal: 1.6.2.3

Reaction with $(GeH_2)_n$: 1.6.3.3.3

Reaction with $GeCl_2$: 1.6.3.3.3

Reaction with GeO : 1.6.3.3.3

Reaction with $(CH_3)_3Ge[Ge(CH_3)_2]_n^*$
 $Ge(CH_3)_3$: 1.6.3.3.3

Reaction with $C_6F_5HgCH_3$: 1.6.3.1.3

Reaction with $Ir(NO)[P(C_6H_5)_3]_3$:
1.5.3.1.3

Reaction with cis-
 $M(N_2)_2[P(CH_3)_2C_6H_5]_4$ ($M = Mo, W$):
1.5.3.1.3

Reaction with $Os(NO)Cl(CO)[P(C_6^*H_5)_3]_2$: 1.5.3.1.3

Reaction with $Os(NO)_2[P(C_6H_5)_2]$:
1.5.3.1.3

Reaction with $(C_6H_5)_2P(O)OCOCH_3$:
1.5.3.2.3

Reaction with $(C_6H_5)_2CPCl$ or $(C_6^*H_5)_2CAsCl$: 1.6.3.1.3

Reaction with $(C_6H_5)_3P=CH_2$: 1.6.3.1.3

Reaction with $[(C_2H_5)_3P]_2Pd[Ge(C_6^*H_5)_3]_2$: 1.6.3.3.3

Reaction with $[(C_2H_5)_3P]_2Pt[Ge(C_6^*H_5)_3][Ge(CH_3)_3]$: 1.6.3.3.3

Reaction with $PtCl(N_2C_6H_5)[P(C_2^*H_5)_3]_2$: 1.5.3.1.3

Reaction with $Pt(C_6H_5C\equiv CC_6H_5)^*$
 $[(C_6H_5)_3P]_2$: 1.6.3.1.3

Reaction with Si at high T: 1.6.6.2

Reaction with $CaSi_2$: 1.6.3.2.1

Reaction with $[(CH_3)_2Si]_6$: 1.6.3.2.3,
1.6.4.2.3

Reaction with $(C_6H_5)_3SiMgBr$: 1.6.3.2.3

Reaction with R_2Sn : 1.6.3.4.3

Reaction with Mg_2Sn : 1.6.3.4.1

Reaction with $(h^5-C_5H_5)_2TiClGe(C_6^*H_5)_3$: 1.6.3.3.3

Reaction with $[h^5-(CH_3)_3C_5]_2TiN_2$:
1.5.3.1.3

Reaction with $[(h^5-C_5H_5)_2TiCl]_2N_2H_2$:
1.5.3.1.3

Reaction with $[(h^5-C_5H_5)_2Ti]_2N_2$:
1.5.3.1.2

Reaction with $WBr_2(NNH_2)[P(CH_3)_2^*C_6H_5]_3$: 1.5.3.1.3

Reaction with CF_3NCl_2 : 1.5.3.1.3

Reaction with $[(CN)_3C]^-$: 1.6.3.1.3

Reaction with C_5H_5Li : 1.6.3.1.3

Reaction with $n-C_4H_9MgBr$: 1.6.3.1.3

Reaction with $(CH_3)_3CCH=CH_2$:
1.6.6.1

Reaction with amides: 1.5.3.1.3

Reaction with group-IIIB amides:
1.5.3.1.3

Reaction with with group-IVB amides:
1.5.3.1.3

Reaction with group-VB amides:
1.5.3.1.3

Reaction with nitriles: 1.5.6.1

Reaction with metal germanides:
1.6.3.3.3

Reaction with amines: 1.5.3.1.2

ClHO₄

HClO₄

Preparation of UH_3 : 1.12.4.2

ClH₂N

NH₂Cl

Formation: 1.5.3.1.2

Reduction to NH_3 : 1.5.3.1.1

ClH₃Si

SiH₃Cl

Reduction of $LiAlD_4$: 1.6.7.1.2

ClH₄N

NH₄Cl

Formation of $AcCl_3$: 1.12.4.2

Protonation of Mg-Si alloys: 1.6.3.2.2

Reaction with organostannides: 1.6.3.4.2

ClH₄P

PH₄Cl

Formation: 1.5.3.2.3

ClH₅*B₂

ClH_8^*B_5
 $\text{ClH}_8\text{Ti}^*\text{B}_2$
 $\text{ClIrNO}_2\text{P}^*\text{C}_{28}\text{H}_{22}$
 $\text{ClIrNP}_2^*\text{C}_{37}\text{H}_{31}$
 $\text{ClIrO}^*\text{C}_{37}\text{H}_{30}\text{As}_2$
 $\text{ClIrOP}^*\text{C}_{19}\text{H}_{15}$
 $\text{ClIrOP}_2^*\text{C}_7\text{H}_{18}$
 $\text{ClIrOP}_2^*\text{C}_{13}\text{H}_{30}$
 $\text{ClIrOP}_2^*\text{C}_{19}\text{H}_{42}$
 $\text{ClIrOP}_2^*\text{C}_{33}\text{H}_{38}$
 $\text{ClIrOP}_2^*\text{C}_{37}\text{H}_{30}$
 $\text{ClIrOP}_2^*\text{C}_{37}\text{H}_{32}$
 $\text{ClIrOP}_2^*\text{C}_{37}\text{H}_{66}$
 $\text{ClIrOP}_2^*\text{C}_{43}\text{H}_{42}$
 $\text{ClIrOP}_4^*\text{C}_{13}\text{H}_{32}$
 $\text{ClIrO}_7\text{P}_2^*\text{C}_{37}\text{H}_{30}$
 $\text{ClIrO}_7\text{P}_2^*\text{C}_{39}\text{H}_{30}$
 $\text{ClIrP}_2^*\text{C}_{21}\text{H}_{46}$
 $\text{ClIrP}_2^*\text{C}_{22}\text{H}_{48}$
 $\text{ClIrP}_2^*\text{C}_{26}\text{H}_{30}$
 $\text{ClIrP}_2^*\text{C}_{37}\text{H}_{30}$
 $\text{ClIrP}_3^*\text{C}_{12}\text{H}_{51}\text{B}_{30}$
 $\text{ClIrP}_3^*\text{C}_{36}\text{H}_{37}$
 $\text{ClIrP}_3^*\text{C}_{36}\text{H}_{39}$
 $\text{ClIrP}_3^*\text{C}_{54}\text{H}_{45}$
 $\text{ClIrP}_4^*\text{C}_{54}\text{H}_{48}$
 $\text{ClIrSi}^*\text{C}_{16}\text{H}_{32}$
 $\text{ClLi}^*\text{C}_8\text{H}_9\text{Al}$
 $\text{ClMg}^*\text{C}_2\text{H}_5$
 $\text{ClMg}^*\text{C}_3\text{H}_7$
 $\text{ClMg}^*\text{C}_6\text{H}_{11}$
 $\text{ClMgN}_2\text{Ti}^*\text{C}_{10}\text{H}_{10}$
 $\text{ClMgN}_2\text{Ti}_2^*\text{C}_{20}\text{H}_{20}$
 $\text{ClMnO}_2\text{Si}^*\text{C}_{20}\text{H}_{18}$
 $\text{ClMo}^*\text{C}_{33}\text{H}_{25}$
 $\text{ClMoN}_3\text{O}_6^*\text{C}_6\text{H}_{13}$
 $\text{ClMoO}_3^*\text{C}_6\text{H}_5$
 $\text{ClMoP}^*\text{C}_{27}\text{H}_{26}$
 $\text{ClN}^*\text{C}_6\text{H}_{16}$
 $\text{ClNOP}_2\text{Pt}^*\text{C}_{16}\text{H}_{36}$
 $\text{ClNOP}_2\text{Pt}^*\text{C}_{43}\text{H}_{36}$
 $\text{ClNO}_2\text{OsP}_2^*\text{C}_{37}\text{H}_{30}$
 $\text{ClNO}_3^*\text{C}_7\text{H}_4$
 $\text{ClNO}_6\text{PS}^*\text{C}_{18}\text{H}_{13}$
 $\text{ClNP}^*\text{C}_{18}\text{H}_{17}$
 $\text{ClNP}_2\text{Pt}^*\text{C}_{18}\text{H}_{36}$
 $\text{ClNP}_2\text{Pt}^*\text{C}_{42}\text{H}_{36}$
 $\text{ClNP}_2\text{Rh}^*\text{C}_{47}\text{H}_{47}$
 $\text{ClNP}_2\text{Rh}^*\text{C}_{47}\text{H}_{49}$
 $\text{ClNSi}^*\text{C}_4\text{H}_{12}$
 $\text{ClN}_2\text{O}_2\text{W}^*\text{C}_5\text{H}_5$
 $\text{ClN}_2\text{P}^*\text{C}_4\text{H}_{12}$

$\text{ClN}_2\text{P}_2\text{Pt}^*\text{C}_{18}\text{H}_{35}$
 $\text{ClN}_2\text{P}_2\text{Rh}^*\text{C}_{46}\text{H}_{49}$
 $\text{ClN}_2\text{P}_2\text{Rh}^*\text{C}_{46}\text{H}_{51}$
 $\text{ClN}_2\text{P}_3\text{W}^*\text{C}_{24}\text{H}_{36}\text{Br}_2$
 $\text{ClN}_2\text{P}_4\text{W}^*\text{C}_{53}\text{H}_{52}\text{Br}$
 $\text{ClN}_3\text{P}_3^*\text{C}_{25}\text{H}_{24}\text{Au}$
 $\text{ClN}_3\text{Si}_6\text{Th}^*\text{C}_{18}\text{H}_{54}$
 $\text{ClN}_4\text{O}_4\text{Rh}^*\text{C}_{26}\text{H}_{29}$
 ClNaO_2
 NaClO_2
 Reaction with phosphorus to form
 $\text{Na}_2[\text{H}_2\text{P}_2\text{O}_4]_2$: 1.5.6.2
 $\text{ClNiP}_2^*\text{C}_{36}\text{H}_{67}$
 ClO^*CAu
 $\text{ClO}^*\text{C}_2\text{H}_3$
 $\text{ClOOSp}_3^*\text{C}_{55}\text{H}_{46}$
 $\text{ClOP}^*\text{C}_5\text{H}_{10}$
 $\text{ClOP}^*\text{C}_8\text{H}_{18}$
 $\text{ClOP}^*\text{C}_{10}\text{H}_{10}$
 $\text{ClOP}^*\text{C}_{10}\text{H}_{14}$
 $\text{ClOP}^*\text{C}_{12}\text{H}_{10}$
 $\text{ClOP}^*\text{C}_{14}\text{H}_{14}$
 $\text{ClOP}_2\text{Rh}^*\text{C}_{37}\text{H}_{30}$
 $\text{ClOP}_3\text{Ru}^*\text{C}_{31}\text{H}_{46}$
 $\text{ClOZr}^*\text{C}_{11}\text{H}_{11}$
 $\text{ClO}_2^*\text{C}_2\text{H}_6\text{B}$
 $\text{ClO}_2\text{P}^*\text{C}_2\text{H}_6$
 $\text{ClO}_2\text{P}_2\text{Pt}^*\text{C}_{13}\text{H}_{31}$
 $\text{ClO}_2\text{Si}^*\text{C}_2\text{H}_7$
 $\text{ClO}_2\text{Si}^*\text{C}_4\text{H}_{11}$
 $\text{ClO}_7\text{Os}_2\text{P}_2^*\text{C}_{39}\text{H}_{31}$
 $\text{ClP}^*\text{C}_2\text{H}_6$
 $\text{ClP}^*\text{C}_2\text{H}_8$
 $\text{ClP}^*\text{C}_{12}\text{H}_{10}$
 $\text{ClP}^*\text{C}_{13}\text{H}_{10}$
 $\text{ClP}^*\text{C}_{19}\text{H}_{18}$
 $\text{ClPRhSi}^*\text{C}_{36}\text{H}_{31}$
 $\text{ClP}_2\text{IrS}^*\text{C}_{36}\text{H}_{32}$
 $\text{ClP}_2\text{Pt}^*\text{C}_{12}\text{H}_{31}$
 $\text{ClP}_2\text{Pt}^*\text{C}_{14}\text{H}_{35}$
 $\text{ClP}_2\text{Pt}^*\text{C}_{15}\text{H}_{37}$
 $\text{ClP}_2\text{Pt}^*\text{C}_{28}\text{H}_{47}$
 $\text{ClP}_2\text{Pt}^*\text{C}_{36}\text{H}_{31}$
 $\text{ClP}_2\text{Rh}^*\text{C}_{21}\text{H}_{44}$
 $\text{ClP}_2\text{Rh}^*\text{C}_{21}\text{H}_{46}$
 $\text{ClP}_2\text{RhS}^*\text{C}_{36}\text{H}_{32}$
 $\text{ClP}_2\text{RhS}^*\text{C}_{46}\text{H}_{50}$
 $\text{ClP}_2\text{RhS}^*\text{C}_{46}\text{H}_{52}$
 $\text{ClP}_2\text{Ru}^*\text{C}_{16}\text{H}_{33}$
 $\text{ClP}_2\text{Ru}^*\text{C}_{41}\text{H}_{35}$
 $\text{ClP}_3\text{Rh}^*\text{C}_{54}\text{H}_{45}$
 $\text{ClP}_3\text{Rh}^*\text{C}_{54}\text{H}_{47}$

$\text{ClP}_3\text{Rh}^*\text{C}_{63}\text{H}_{63}$
 $\text{ClP}_3\text{Rh}^*\text{C}_{63}\text{H}_{65}$
 $\text{ClP}_3\text{Ru}^*\text{C}_{54}\text{H}_{46}$
 $\text{ClP}_3\text{Si}_4^*\text{C}_{12}\text{H}_{36}$
 $\text{ClP}_4\text{Ru}^*\text{C}_{13}\text{H}_{39}$
 $\text{ClPb}^*\text{C}_3\text{H}_9$
 $\text{ClPb}^*\text{C}_6\text{H}_{15}$
 $\text{ClPb}^*\text{C}_9\text{H}_{21}$
 $\text{ClPb}^*\text{C}_{12}\text{H}_{27}$
 $\text{ClPt}^*\text{C}_{24}\text{H}_{55}\text{As}_2$
 $\text{ClRe}^*\text{C}_{10}\text{H}_{12}$
 $\text{ClRh}^*\text{C}_{54}\text{H}_{45}$
 $\text{ClRhP}_4^*\text{C}_{20}\text{H}_{49}$
 $\text{ClSb}^*\text{C}_2\text{H}_6$
 $\text{ClSb}^*\text{C}_8\text{H}_{18}$
 $\text{ClSb}^*\text{C}_{12}\text{H}_{10}$
 $\text{ClSb}^*\text{C}_{12}\text{H}_{22}$
 $\text{ClSi}^*\text{C}_2\text{H}_7$
 $\text{ClSi}^*\text{C}_3\text{H}_9$
 $\text{ClSi}^*\text{C}_4\text{H}_{11}$
 $\text{ClSi}^*\text{C}_6\text{H}_{15}$
 $\text{ClSi}^*\text{C}_{12}\text{H}_{11}$
 $\text{ClSi}^*\text{C}_{18}\text{H}_{15}$
 $\text{ClSi}^*\text{C}_{18}\text{H}_{39}$
 $\text{ClSi}_2^*\text{C}_5\text{H}_{15}$
 $\text{ClSi}_6^*\text{C}_{12}\text{H}_{37}$
 $\text{ClSn}^*\text{C}_2\text{H}_7$
 $\text{ClSn}^*\text{C}_3\text{H}_9$
 $\text{ClSn}^*\text{C}_4\text{H}_{11}$
 $\text{ClSn}^*\text{C}_6\text{H}_{15}$
 $\text{ClSn}^*\text{C}_8\text{H}_{19}$
 $\text{ClSn}^*\text{C}_9\text{H}_{21}$
 $\text{ClSn}^*\text{C}_{12}\text{H}_{11}$
 $\text{ClSn}^*\text{C}_{12}\text{H}_{27}$
 $\text{ClSn}^*\text{C}_{18}\text{H}_{15}$
 $\text{ClW}^*\text{C}_5\text{H}_8$
ClZr

ZrCl

Reaction with H_2 : 1.12.8.2.5

$\text{ClZr}^*\text{C}_5\text{H}_6$
 $\text{ClZr}^*\text{C}_{10}\text{H}_{11}$
 $\text{ClZr}^*\text{C}_{11}\text{H}_{13}$

Cl₂

Reaction with $(\text{C}_6\text{H}_5)_3\text{PNH}$: 1.5.3.1.3

Cl_2^*Ba
 $\text{Cl}_2^*\text{CH}_3\text{As}$
 $\text{Cl}_2^*\text{CH}_3\text{Bi}$
 $\text{Cl}_2^*\text{C}_{13}\text{H}_{11}\text{As}$
 $\text{Cl}_2^*\text{C}_{18}\text{H}_{15}\text{Bi}$
 $\text{Cl}_2^*\text{C}_{18}\text{H}_{17}\text{As}$
Cl₂Co

CoCl₂

Reaction with $\text{Na}[\text{BH}_4]$: 1.10.9

$\text{Cl}_2\text{CuN}_2^*\text{C}_{16}\text{H}_{53}\text{B}_{10}$

Cl₂FP

PFC1₂

Protonation in strong acid: 1.5.3.2.2,
1.5.3.2.3

$\text{Cl}_2\text{F}_3\text{N}^*\text{C}$

$\text{Cl}_2\text{F}_3\text{P}^*\text{C}$

$\text{Cl}_2\text{F}_5\text{N}^*\text{C}_2$

$\text{Cl}_2\text{F}_6\text{P}_5\text{Pt}_2^*\text{C}_{50}\text{H}_{45}$

Cl₂Fe

FeCl₂

Reaction with $\text{Na}[\text{BH}_4]$: 1.10.9

$\text{Cl}_2\text{FeP}_4^*\text{C}_{20}\text{H}_{48}$

$\text{Cl}_2\text{FeP}_4^*\text{C}_{52}\text{H}_{48}$

$\text{Cl}_2\text{Fe}_2\text{GeO}_4^*\text{C}_{14}\text{H}_{10}$

Cl₂GaH

HGaCl₂

Formation: 1.7.3.2

Cl₂Ge

GeCl₂

Reaction with HCl: 1.6.3.3.3

$\text{Cl}_2\text{Ge}^*\text{C}_2\text{H}_6$

$\text{Cl}_2\text{Ge}^*\text{C}_4\text{H}_{10}$

$\text{Cl}_2\text{Ge}^*\text{C}_{12}\text{H}_{10}$

Cl₂GeH₂

GeH₂Cl₂

Reduction by $\text{Li}[\text{AlH}_4]$: 1.6.5.3.1

$\text{Cl}_2\text{GeP}_2\text{Pt}^*\text{CH}_{44}$

$\text{Cl}_2\text{Ge}_2^*\text{C}_{12}\text{H}_{28}$

$\text{Cl}_2\text{H}^*\text{B}$

$\text{Cl}_2\text{IrOP}_2^*\text{C}_{37}\text{H}_{31}$

$\text{Cl}_2\text{IrP}_3^*\text{C}_{18}\text{H}_{46}$

$\text{Cl}_2\text{Ir}_2^*\text{C}_{16}\text{H}_{24}$

$\text{Cl}_2\text{Ir}_2^*\text{C}_{20}\text{H}_{17}$

$\text{Cl}_2\text{Ir}_2^*\text{C}_{32}\text{H}_{56}$

$\text{Cl}_2\text{Mg}_2\text{NO}_5\text{Ti}^*\text{C}_{13}\text{H}_{24}$

$\text{Cl}_2\text{Mg}_2\text{NO}_5\text{V}^*\text{C}_{13}\text{H}_{24}$

$\text{Cl}_2\text{N}^*\text{C}_7\text{H}_7$

$\text{Cl}_2\text{N}^*\text{C}_7\text{H}_8\text{B}$

$\text{Cl}_2\text{NOPPt}^*\text{C}_{27}\text{H}_{26}$

$\text{Cl}_2\text{NO}_2\text{OsP}_2^*\text{C}_{37}\text{H}_{31}$

$\text{Cl}_2\text{NO}_4\text{PS}^*\text{C}_{12}\text{H}_8$

$\text{Cl}_2\text{NPPT}^*\text{C}_{25}\text{H}_{20}$

$\text{Cl}_2\text{NP}_2\text{Re}^*\text{C}_{43}\text{H}_{38}$

$\text{Cl}_2\text{N}_2\text{O}_2\text{OsP}_2^*\text{C}_{36}\text{H}_{32}$

$\text{Cl}_2\text{N}_2\text{P}_2\text{Pt}^*\text{C}_{18}\text{H}_{36}$

$\text{Cl}_2\text{N}_2\text{Ti}_2^*\text{C}_{20}\text{H}_{22}$

$\text{Cl}_2\text{N}_4\text{O}_5\text{Ru}^*\text{C}_{25}\text{H}_{16}$

$\text{Cl}_2\text{Nb}^*\text{C}_{10}\text{H}_{10}$

$\text{Cl}_2\text{NiP}_2^*\text{C}_{36}\text{H}_{66}$

$\text{Cl}_2\text{OP}^*\text{C}_6\text{H}_5$

$\text{Cl}_2\text{OSi}^*\text{C}_2\text{H}_6$

$\text{Cl}_2\text{O}_2\text{Si}^*\text{C}_4\text{H}_{10}$

- $\text{Cl}_2\text{O}_{12}\text{P}_4\text{Ru}^*\text{C}_{24}\text{H}_{60}$
 $\text{Cl}_2\text{OsP}_3^*\text{C}_{30}\text{H}_{43}$
 $\text{Cl}_2\text{P}^*\text{CH}_3$
 $\text{Cl}_2\text{P}^*\text{C}_2\text{H}_5$
 $\text{Cl}_2\text{P}^*\text{C}_3\text{H}_7$
 $\text{Cl}_2\text{P}^*\text{C}_4\text{H}_9$
 $\text{Cl}_2\text{P}^*\text{C}_6\text{H}_5$
 $\text{Cl}_2\text{P}^*\text{C}_7\text{H}_7$
 $\text{Cl}_2\text{P}^*\text{C}_{13}\text{H}_{11}$
 $\text{Cl}_2\text{P}_2\text{Pt}^*\text{C}_{12}\text{H}_{30}$
 $\text{Cl}_2\text{P}_3\text{Rh}^*\text{C}_{42}\text{H}_{45}$
 $\text{Cl}_2\text{P}_3\text{Ru}^*\text{C}_{54}\text{H}_{45}$
 $\text{Cl}_2\text{P}_4\text{Pt}^*\text{C}_{50}\text{H}_{44}$
 $\text{Cl}_2\text{P}_4\text{Ta}^*\text{C}_{12}\text{H}_{32}$
 Cl_2Pb
 PbCl_2
 Structure: 1.8.3
 $\text{Cl}_2\text{Pb}^*\text{C}_2\text{H}_6$
 $\text{Cl}_2\text{Pb}^*\text{C}_4\text{H}_{10}$
 $\text{Cl}_2\text{Pb}^*\text{C}_6\text{H}_{14}$
 $\text{Cl}_2\text{Pb}^*\text{C}_8\text{H}_{18}$
 $\text{Cl}_2\text{Pb}^*\text{C}_{12}\text{H}_{22}$
 $\text{Cl}_2\text{Rh}_2^*\text{C}_{14}\text{H}_{16}$
 $\text{Cl}_2\text{Rh}_2\text{P}_4^*\text{C}_{84}\text{H}_{84}$
 $\text{Cl}_2\text{Sb}^*\text{CH}_3$
 $\text{Cl}_2\text{Sb}^*\text{C}_2\text{H}_5$
 $\text{Cl}_2\text{Sb}^*\text{C}_4\text{H}_9$
 $\text{Cl}_2\text{Si}^*\text{CH}_4$
 $\text{Cl}_2\text{Si}^*\text{C}_2\text{H}_6$
 $\text{Cl}_2\text{Si}^*\text{C}_4\text{H}_{10}$
 $\text{Cl}_2\text{Si}^*\text{C}_9\text{H}_{12}$
 $\text{Cl}_2\text{Si}^*\text{C}_{12}\text{H}_{10}$
 $\text{Cl}_2\text{Si}_2^*\text{C}_{12}\text{H}_{28}$
 Cl_2Sn
 SnCl_2
 Reaction with H_2 : 1.6.2.4
 Reduction by NaBH_4 in H_2O : 1.6.5.4.1
 $\text{Cl}_2\text{Sn}^*\text{C}_2\text{H}_6$
 $\text{Cl}_2\text{Sn}^*\text{C}_4\text{H}_{10}$
 $\text{Cl}_2\text{Sn}^*\text{C}_{12}\text{H}_{10}$
 $\text{Cl}_2\text{Sn}_2^*\text{C}_8\text{H}_{18}$
 $\text{Cl}_2\text{Ti}^*\text{C}_4\text{H}_{10}$
 Cl_2V
 VCl_2
 Reaction with N_2 , Mg and CO_2 :
 1.5.3.1.1
 Cl_2Zn
 ZnCl_2
 Reduction by NaH to give ZnH_2 : 1.9.4.1
 $\text{Cl}_2\text{Zr}^*\text{C}_{10}\text{H}_{10}$
 Cl_3^*Ac
 Cl_3Ac
 Formation: 1.12.4.1
 Cl_3^*Al
 Cl_3^*As
 Cl_3^*B
 Cl_3^*Bi
 Cl_3Ga
 GaCl_3
 Reaction with H^- : 1.7.4.3
 $\text{Cl}_3\text{Ge}^*\text{CH}_3$
 $\text{Cl}_3\text{Ge}^*\text{C}_2\text{H}_5$
 $\text{Cl}_3\text{Ge}^*\text{C}_6\text{H}_5$
 Cl_3GeH
 Formation: 1.6.2.3, 1.6.3.3.3
 Reaction with $\text{Li}[\text{AlH}_4]$: 1.6.5.3.1
 Reaction with $\text{Li}[\text{AlD}_4]$: 1.6.7.1.3
 $\text{Cl}_3\text{GeO}^*\text{C}_4\text{H}_{11}$
 Cl_3HInLi
 LiInCl_3H
 Formation: 1.7.5.2
 Cl_3HSi
 HSiCl_3
 Formation: 1.6.2.2, 1.6.3.2.3
 Industrial formation: 1.6.6.2
 Reduction by NaAlH_4 : 1.6.5.2.1
 Reduction of phosphorus compounds:
 1.5.4.2.2
 $\text{Cl}_3\text{H}_4\text{InLi}^*\text{Al}$
 $\text{Cl}_3\text{H}_4\text{InLi}^*\text{B}$
 Cl_3In
 InCl_3
 Reaction with H^- : 1.7.4.4
 $\text{Cl}_3\text{IrNOP}_2^*\text{C}_{36}\text{H}_{33}$
 $\text{Cl}_3\text{IrP}_3^*\text{C}_{18}\text{H}_{45}$
 Cl_3NORu
 $\text{Ru}(\text{NO})\text{Cl}_3$
 Reaction with KOH , EtOH and PPh_3 :
 1.10.8
 $\text{Cl}_3\text{NP}_2\text{Re}^*\text{C}_{12}\text{H}_{23}$
 $\text{Cl}_3\text{NP}_2\text{Re}^*\text{C}_{43}\text{H}_{37}$
 $\text{Cl}_3\text{OGe}^*\text{C}_4\text{H}_{11}$
 Cl_3OP
 $\text{P}(\text{O})\text{Cl}_3$
 Reaction with LiH : 1.5.4.2.1
 $\text{Cl}_3\text{OP}^*\text{C}_{14}\text{H}_{15}\text{B}$
 $\text{Cl}_3\text{OP}_2\text{Re}^*\text{C}_{20}\text{H}_{30}$
 $\text{Cl}_3\text{OsP}_3^*\text{C}_{42}\text{H}_{72}$
 Cl_3P
 PCl_3
 Alcoholysis to form alkylphosphonates:
 1.5.6.2
 Hydrolysis: 1.5.3.2.1, 1.5.3.2.3, 1.5.6.2
 Protonation in strong acid: 1.5.3.2.2,
 1.5.3.2.3
 Reaction with D_2O : 1.5.7.1.2

Cl₃P *cont.*

- Reaction with LiH: 1.5.4.2.1
- Reduction by Li[AlD₄]: 1.5.7.1.2
- Reduction by Li[AlH₄]: 1.5.5.2.1

Cl₃P*C₁₂H₁₀**Cl₃PS***C₁₄H₁₅B**Cl₃P₃Re***C₂₄H₃₃**Cl₃P₃Re***C₃₀H₄₅**Cl₃Rh****RhCl₃**

- Reaction with NaBH₄: 1.10.9
- Reaction with ethanolic KOH and PPh₃: 1.10.8

Cl₃Ru**RuCl₃**

- Reaction with ethanolic KOH and PPh₃: 1.10.8

Cl₃Sb**SbCl₃**

- Reduction by Li[BD₄]: 1.5.7.1.4
- Reduction by Li[BH₄], Li[AlH₄]: 1.5.5.4

Cl₃Sc**ScCl₃**

- Preparation of ScH₂: 1.12.4.1

Cl₃Si*CH₃**Cl₃Si***C₂H₅**Cl₃Si***C₃H₅**Cl₃Si***C₃H₁₁**Cl₃Si***C₆H₅**Cl₃Si***C₆H₁₃**Cl₃Sn***CH₃**Cl₃Sn***C₂H₅**Cl₃Sn***C₄H₉**Cl₃Sn***C₆H₅**Cl₃Tl****TlCl₃**

- Reaction with H⁻: 1.7.4.5

Cl₄*B₂**Cl₄*C****Cl₄Ge****GeCl₄**

- Reaction with (C₂H₅)₃GeH: 1.6.4.3.1
- Reaction with alkylsilanes: 1.6.4.3.1
- Reduction by Li[AlD₄]: 1.6.7.1.3
- Reduction by (i-C₄H₉)₂AlH: 1.6.4.3.1
- Reduction by Na[BH₄]: 1.6.5.3.1
- Reduction by [(CH₃)₂SiH]₂O: 1.6.4.3.1
- Reduction by LiH: 1.6.4.3.1

Cl₄H₂N₂O₂P₂**[Cl₂P(O)NH]₂**

- Formation: 1.5.3.1.3

Cl₄IrP₃*C₉H₂₈**Cl₄Ir₂***C₁₆H₂₆**Cl₄Li***Al**Cl₄MoP₂***C₂₆H₂₆**Cl₄N₃P₃***CH₄**Cl₄N₃P₃***C₂H₆**Cl₄N₃P₃***C₃H₈**Cl₄Ni₂***C₁₆H₂₄**Cl₄P₂W***C₁₆H₂₂**Cl₄P₂W***C₂₈H₃₀**Cl₄P₃W***C₉H₂₇**Cl₄P₃W***C₂₄H₃₃**Cl₄P₆Ru₂***C₆₀H₉₀**Cl₄Pd₂***C₅₆H₄₀**Cl₄Si****SiCl₄**

- Reaction with H₂: 1.6.2.2
- Reduction by Al-H₂-NaH in AlCl₃-*NaCl: 1.6.4.2.1
- Reduction by B₂H₆: 1.6.4.2.1
- Reduction by Li[AlH₄]: 1.6.5.2.1
- Reduction by Li[BH₄]: 1.6.5.2.1
- Reduction by LiH: 1.6.4.2.1
- Reduction by NaH and (C₂H₅)₃B: 1.6.4.2.1

Cl₄Si*C₂H₄**Cl₄Sn****SnCl₄**

- Reduction by Li[AlD₄]: 1.6.7.1.4
- Reduction by Li[AlH₄]: 1.6.5.4.1
- Reduction by Li[(t-C₄H₉O)₃AlH]: 1.6.5.4.1

Cl₅NOP₂**Cl₃PNP(O)Cl₂**

- Reaction with alcohols: 1.5.3.1.3

Cl₅NSb*C₆H₉**Cl₅Nb****NbCl₅**

- Reaction with H₂: 1.10.3.2

Cl₅Re**ReCl₅**

- Reaction with Na[BH₄] and Na[C₅H₅]: 1.10.9

Cl₅Sb**SbCl₅**

- Reduction by Li, Na, K[BH₄]: 1.5.5.4

Cl₅Ta**TaCl₅**

- Reaction with Li[AlH₄] and LiC₅H₄Me: 1.10.7.2
- Reaction with H₂ and Me₂P(CH₂)₂P*: 1.10.3.2

- Cl₆Ga₂**
Ga₂Cl₆
Reduction by (CH₃)₃SiH: 1.7.3.2
- Cl₆GeSi**
Cl₃GeSiCl₃
Reduction by LiAlH₄: 1.6.5.3.1
- Cl₆H₂Pt**
H₂PtCl₆
Catalyst in SiCl₃D exchange with CH₃*
Cl₂SiH: 1.6.7.2.2
- Cl₆H₁₂IrNa₂O₆**
Na₂IrCl₆·6 H₂O
Reaction with NaBH₄: 1.10.9
Reaction with alcoholic KOH and
PPh₃: 1.10.8
- Cl₆H₁₂Na₂O₆Os**
Na₂OsCl₆·6 H₂O
Reaction with alcoholic PPh₃: 1.10.8
- Cl₆IrH₂**
H₂[IrCl₆]
Reaction with EtOH and diene: 1.10.8
- Cl₆IrNa₂**
Na₂[IrCl₆]
Reaction with Na[BH₄]: 1.10.9
- Cl₆N₂P₂*C₂**
- Cl₆N₃P₃**
(NPCl₂)₃
Conversion to (NPCl₂)₂NP(H)CH₃:
1.5.3.2.3
Conversion to (NPCl₂)₂NP(H)C₂H₅:
1.5.3.2.3
Conversion to (NPCl₂)₂NP(H)C₃H₇-n:
1.5.3.2.3
- Cl₆OSi₂**
(SiCl₃)₂O
Reduction by Li[AlD₄]: 1.6.7.1.2
Reduction by Li[AlH₄]: 1.6.5.2.2
- Cl₆P₄Ta₂*C₁₂H₃₈**
- Cl₆Si₂**
Si₂Cl₆
Reduction by Li[AlD₄]: 1.6.7.1.2
Reduction by Li[AlH₄]: 1.6.5.2.1
Reduction by AlH₃: 1.6.4.2.1
- Cl₇FNP*C₂H₂**
- Cl₇NP*C₂H**
- Cl₈Si₃**
Si₃Cl₈
Reduction by Li[AlH₄]: 1.6.5.2.1
- Cl₉O₉Os₃Si₃*C₉H₃**
- Cl₁₀Si₄**
Si₄Cl₁₀
Reduction by Li[AlH₄]: 1.6.5.2.1
- Cl₁₂Si₅**
Si₅Cl₁₂
Reduction by Li[AlH₄]: 1.6.5.2.1
- Co**
Catalysis of CO reaction with H₂:
1.6.6.1
Oxidative addition of CH₄: 1.10.5.3
Reaction with PF₃ and H₂: 1.10.2
Reaction with CO and H₂: 1.10.2
- Co*C₈H₁₃**
- Co*C₁₀H₁₅**
- Co*Cl₂**
- CoF₆P₃*C₁₁H₂₄**
- CoF₆P₃*C₁₆H₃₄**
- CoF₈P₃*C₁₄H₃₂B₂**
- CoF₁₂HP₄**
CoH(PF₃)₄
Formation: 1.10.2, 1.10.3.2
- CoH₂N₂O₇**
Co[NO₃]₂H₂O
Reaction with Na[BH₄]: 1.10.9
- CoHf**
HfCo
Reaction with H₂: 1.12.8.1.3
Structure: 1.12.8.1.3
- CoKO₁₃Ru₃*C₁₃**
- CoN₂O₂*C₇H₇**
- CoN₂O₂*C₉H₁₁**
- CoN₂O₂*C₁₁H₁₅**
- CoN₂P₃*C₅₄H₄₆**
- CoN₄O₄*C₂₀H₄₁Cl**
- CoN₄O₄*C₂₀H₄₂**
- CoN₄O₄P*C₂₀H₄₂**
- CoO₃P*C₂₁H₁₆**
- CoO₄*C₄H**
- CoO₆*C₁₅H₂₁**
- CoO₆P*C₂₁H₁₆**
- CoO₁₂P₄*C₃₆H₈₅**
- CoO₁₂P₄*C₇₂H₆₁**
- CoO₁₂Ru₃*C₁₂H₃**
- CoO₁₃Ru₃*C₁₃H**
- CoP₂*C₁₁H₂₃**
- CoP₂*C₁₆H₃₃**
- CoP₃*C₅₄H₄₈**
- CoP₄*C₃₂H₄₅**
- CoTi**
TiCo
Reaction with H₂: 1.12.8.1.3
- CoZr**
ZrCo
Structure: 1.12.8.1.3
- Co₂*C₈O₈**

- Co₂*Ce**
Co₂Dy
 DyCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂Er
 ErCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂F₆P₃*C₁₄H₂₃
Co₂Gd
 GdCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂Ho
 HoCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂N₆O₄*C₃₄H₃₀
Co₂O₁₂Ru₂*C₁₂H₂
Co₂O₁₃Ru₂*C₁₃
Co₂P₂*C₁₄H₂₂
Co₂Pr
 PrCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂Sc
 ScCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂Sm
 SmCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂Tb
 TbCo₂
 Reaction with H₂: 1.12.8.1.2
Co₂Y
 YCo₂
 Reaction with H₂: 1.12.8.1.2
Co₃F₆O₉P*C₁₃H₆
Co₃FeNO₁₂P*C₂₂H₂₇
Co₃FeO₁₂*C₁₂H
Co₃FeO₁₄P*C₂₀H₂₂
Co₃NaO₁₂Os*C₁₂
Co₃O₉*C₁₂H₅
Co₃O₉*C₁₃H₅
Co₃O₉*C₁₃H₇
Co₃O₉*C₁₇H₇
Co₃O₁₀*C₁₂H₃
Co₃O₁₀*C₁₃H₅
Co₃O₁₀*C₁₇H₅
Co₃O₁₂Os*C₁₂H
Co₅Gd
 GdCo₅
 Reaction with H₂: 1.12.8.1.1
Co₅La
 LaCo₅
 Reaction with H₂: 1.12.8.1.1
Co₅Nd
 NdCo₅
 Reaction with H₂: 1.12.8.1.1
Co₅Pr
 PrCo₅
 Reaction with H₂: 1.12.8.1.1
Co₅Sm
 SmCo₅
 Reaction with H₂: 1.12.8.1.1
Co₅Th
 ThCo₅
 Reaction with H₂: 1.12.8.1.1
Co₅Y
 YCo₅
 Reaction with H₂: 1.12.8.1.1
Co₆KO₁₅*C₁₅H
Co₆K₂O₁₅*C₁₅
Co₇Fe₂O₃₀*C₄₂H₃₆
CrD₆O₃*C₉
CrF₆O₅*C₉H₆As₂
CrF₆O₄P*C₇H
CrF₆O₅P₂*C₉H₆
CrF₆PO₅*C₉H₆As
CrF₉P₃*C₈H₁₂
CrFe
 Fe-Cr
 Catalyst for H₂ reaction with graphite:
 1.6.2.1.1
CrH
 Formation: 1.12.7
CrH₂
 Formation: 1.12.7
CrO₂P*C₂₆H₂₁
CrO₃*C₈H₆
CrO₃*C₉H₆
CrO₃*C₁₂H₁₂
CrO₅*C₇H₇As
CrO₅P₂*C₉H₁₂
CrO₆*C₆
CrPO₅*C₇H₇
Cr₂*B
Cr₂KO₁₀*C₁₀H
Cr₂NO₁₀*C₁₈H₂₁
Cr₂N₂O₁₀*C₂₆H₄₀
Cr₃O₃-Zn
 Zn-Cr₂O₃
 Catalysis of CO-H₂ reaction: 1.6.2.1.2
Cr₂O₆*C₁₆H₁₀
Cr₂Ti
 TiCr₂
 Reaction with H₂: 1.12.8.1.2
Cr₂Zr
 ZrCr₂
 Reaction with H₂: 1.12.8.1.2
Cs*Cl
CsF
 Reaction with H₂PF₃: 1.5.3.2.3

- CsF₄H₂P**
Cs[PF₄H₂]
Formation: 1.5.3.2.3
- CsH**
Formation: 1.8.2.2
Reaction with [Ru₂(CO)₃(C₅H₅-h³)₂(C₃H₅-h³)]⁺: 1.6.4.1.4
Reaction with N₂: 1.5.4.1.1
Reaction with red phosphorus: 1.5.4.2.1
- CsH₂N**
CsNH₂
Formation: 1.5.4.1.1
H₂NCS
Reaction with protonic acids: 1.5.3.1.3
- CsH₂P**
CsPH₂
Formation: 1.5.4.2.1
- CsH₄*Al**
Cs₂*C₂
Cs₂HN
[NH]Cs₂
Reaction with protonic acids: 1.5.3.1.3
- Cs₃N**
Reaction with protonic acids: 1.5.3.1.3
- Cu**
Oxidative addition of CH₄: 1.10.5.3
- CuH**
(CuH)_n
Formation: 1.9.3, 1.9.5.1
From CuSO₄ and H₂P(O)OH: 1.9.5.2
Structure: 1.9.1
- CuH₂K**
KCuH₂
Formation: 1.9.5.1
- CuH₂Li**
LiCuH₂
Formation: 1.9.5.1
- CuH₃Li₂**
Li₂CuH₃
Formation and decomposition: 1.9.5.1
- CuH₄*Al**
CuH₄Li₃
Li₃CuH₄
Formation and decomposition: 1.9.5.1
- CuH₅Li₄**
Li₄CuH₅
Formation and decomposition: 1.9.5.1
- CuH₈*B₃**
- CuI**
Reduction by H₂ in liq NH₃: 1.9.5.2
- CuMg₂**
Mg₂Cu
Catalyst for reaction of H₂ with Mg:
1.8.3.2
- CuNP₃*C₅₅H₄₈B**
CuN₂*C₁₆H₅₃B₁₀Cl₂
CuN₂P₂*C₃₈H₃₆B₂
CuO₂P₂*C₂₆H₂₆B
CuO₂P₃*C₅₆H₅₁B
CuO₄S
CuSO₄
Reaction with H₂P(O)OH: 1.9.5.2
- CuP*C₁₈H₁₆**
CuP*C₁₈H₂₃B₃
CuP₂*C₂₆H₂₈B
CuP₂*C₃₆H₃₄B
CuP₂*C₃₆H₃₈B₃
CuP₂*C₃₆H₃₈B₅
CuP₂*C₃₆H₃₉B₆
CuP₃*C₂₄H₃₇B
CuP₃*C₅₄H₄₅Cl
- CuPd**
Pd-Cu
Reaction with H₂: 1.9.1
- Cu₂*C₂**
Cu₂F₄P₄*C₇₂H₆₄B₂
Cu₂H₃Li
LiCu₂H₃
Formation and decomposition: 1.9.5.1
- Cu₂H₁₀*B₁₀**
Cu₂P₄*C₇₂H₇₀B₁₀
Cu₃H₅Li₂
Li₂Cu₃H₅
Formation: 1.9.5.1
- Cu₄F₂₀*C₂₄**
Cu₅*Ca
Cu₅La
LaCu₅
Reaction with H₂: 1.12.8.1.1
- Cu₆P₃*C₅₄H₅₁**
D*Br
D*CH₃
D*C₂H₃
D*C₂H₅
D*C₂H₅
D*C₃H₆Cl
D*C₃H₇
D*C₄H₉
D*C₄H₁₀Al
D*C₆H₅
D*C₇H₇
D*C₈H₁₈Al
D*C₁₀H₇
D*Cl
- DF**
Exchange with C₆H₆ in liq media:
1.6.7.2.1
DGe*C₁₈H₁₅
D*GeH₃

- DGeH₃**
 GeH₃D
 Formation: 1.6.7.3.1
DGeNiP₃*C₆₆H₅₅
 DH₂*As
DH₃Si
 SiH₃D
 Formation: 1.6.7.1.2
 DH₈*B₅
 DH₉*B₄
 DH₁₃*B₁₀
DLi
 LiD
 Reduction of PBr₃: 1.5.7.1.2
 Reduction of (C₆H₅)₃SiCl: 1.6.7.1.2
 Reduction of C₆H₅CH₂Cl: 1.6.7.1.1
DLi*C₆H₁₅B
DN*C₂H₆
DN₃P₃*C₂₅H₂₃
DO*C₂H₅
DP
 (PD)_n
 Formation: 1.5.7.1.2
DP*C₂H₆
DP*C₁₂H₁₀
DSi*C₉H₂₁
DSi*C₁₈H₁₅
DSn*C₆H₁₅
DSn*C₁₂H₂₇
D₂
 Exchange with SiH₄: 1.6.7.2.2
 Exchange with C₃H₈ over Ni: 1.6.7.2.1
 Reaction with N₂: 1.5.7.1.1
 Reduction of C₆H₅ND₂: 1.5.7.1.1
 Reduction of C₆H₅NO: 1.5.7.1.1
 Reduction of C₆H₅CN over Pt: 1.5.7.1.1
D₂*C₂
D₂*C₈H₆Br₂
D₂Fe₂O₄P*C₁₄H₁₀Cl
D₂HN
 ND₂H
 Formation: 1.5.7.1.1
D₂HP
 PHD₂
 Formation: 1.5.7.1.2
D₂H₈*B₄
D₂H₁₂*B₁₀
D₂IrOP₂*C₃₇H₃₁
D₂Mo
 MoD₂
 Formation: 1.12.7
D₂N*C₃H₅
D₂N*C₆H₅
D₂N*C₁₁H₁₅
D₂NSi*C₃H₉
D₂O
 Cleavage of H₃GeAsH₂: 1.6.7.1.3
 Cleavage of H₃SiAsH₂: 1.6.7.1.3
 Exchange with GeH₄: 1.6.7.2.3
 Exchange with [CH₃PH₃]⁺ ion: 1.5.7.2.2
 Exchange with PH₃: 1.5.7.2.2
 Exchange with C₂H₂: 1.6.7.2.1
 Exchange with amines: 1.5.7.2.1
 Exchange with arsines: 1.5.7.2.3
 Reaction with Al₄C₃: 1.6.7.1.1
 Reaction with AlP or Ca₃P₂: 1.5.7.1.2
 Reaction with (CH₃)₃Al: 1.6.7.1.1
 Reaction with Na₃As: 1.6.7.1.3
 Reaction with C₂H₅Li: 1.6.7.1.1
 Reaction with Na₂[C₆H₅P]: 1.5.7.1.2
 Reaction with (C₆H₅)₂PLi: 1.5.7.1.2
 Reaction with PCl₃: 1.5.7.1.2
 Reaction with PI₃: 1.5.7.1.2
 Reaction with P₄: 1.5.7.1.2
 Reaction with Mg₂Si: 1.6.7.1.2
 Reaction with (SiH₃)₂PH: 1.5.7.1.2
 Reaction with Na[[C(CH₃)₃Si]₂N]: 1.5.3.1.3
 Reaction with Mg₂Sn: 1.6.7.1.4
 Reaction with Mg₃N₂: 1.5.7.1.1
 Reaction with alkyl- and arylstannides: 1.6.7.1.4
D₂O*C₃H₆
D₂O*C₇H₆
D₂O*C₈H₈
D₂O₄S
 D₂SO₄
 Exchange with C₂H₄: 1.6.7.2.1
D₂O₁₂Ru₄*C₁₂H₂
D₂P*C₆H₅
D₂PSi*C₂H₇
D₂Si*C₂H₆
D₂Si*C₁₂H₁₀
D₃*Al
D₃*As
D₃*C₇H₅
D₃*C₉H₁₈B
D₃H₁₁K*B₉
D₃IrOP₂*C₂₇H₂₄
D₃N
 ND₃
 Exchange with C₃H₈: 1.6.7.2.1
 Exchange with C₆H₅CH₃: 1.6.7.2.1

- Formation: 1.5.3.1.1, 1.5.7.1.1
 Industrial formation from Mg_3N_2 and acid: 1.5.6.1
 $\text{D}_3\text{O}^*\text{C}_3\text{H}_5$
 $\text{D}_3\text{O}^*\text{C}_7\text{H}_5$
 $\text{D}_3\text{O}_3\text{P}$
 D_3PO_3
 Formation: 1.5.7.1.2
 D_3P
 PD_3
 Formation: 1.5.6.2, 1.5.7.1.2, 1.5.7.2.2
 D_3Sb
 SbD_3
 Formation: 1.5.7.1.4
 D_4^*C
 D_4^*C_2
 D_4Ge
 GeD_4
 Formation: 1.6.7.1.3, 1.6.7.2.3
 $\text{D}_4\text{H}_4^*\text{B}_{10}$
 $\text{D}_4\text{H}_8^*\text{B}_6$
 $\text{D}_4\text{H}_{10}^*\text{B}_{10}$
 $\text{D}_4\text{Li}^*\text{Al}$
 $\text{D}_4\text{Li}^*\text{B}$
 $\text{D}_4\text{N}^*\text{C}_7\text{H}_5$
 $\text{D}_4\text{Na}^*\text{B}$
 $\text{D}_4\text{O}_4\text{P}_2^*\text{Ba}$
 $\text{D}_4\text{O}_{12}\text{Ru}_4^*\text{C}_{12}$
 D_4P_2
 P_2D_4
 Formation: 1.5.7.1.2
 D_4Si
 SiD_4
 Formation: 1.6.7.1.2, 1.6.7.2.2
 D_4Sn
 SnD_4
 Formation: 1.6.7.1.4
 $\text{D}_5\text{H}_9\text{K}^*\text{B}_9$
 D_6^*B_2
 D_6^*C_6
 D_6Ge_2
 Ge_2D_6
 Formation: 1.6.7.1.3
 $\text{D}_6\text{H}_8^*\text{B}_{10}$
 $\text{D}_6\text{Ni}_3\text{P}_3^*\text{C}_{15}\text{H}_{15}$
 $\text{D}_6\text{O}_3^*\text{C}_9\text{Cr}$
 D_6Si_2
 Si_2D_6
 Formation: 1.6.7.1.2
 D_8^*C_3
 D_8^*C_4
- D_8Ge_3
 Ge_3D_8
 Formation: 1.6.7.1.3
 $\text{D}_8\text{H}_6^*\text{B}_{10}$
 D_8Si_3
 Si_3D_8
 Formation: 1.6.7.1.2
 $\text{D}_{10}\text{H}_4^*\text{B}_{10}$
 D_{10}Si_4
 $n\text{-Si}_4\text{D}_{10}$
 Formation: 1.6.7.1.2
 $\text{D}_{12}\text{H}_2^*\text{B}_{10}$
 Dy^*Co_2
 DyFe_2
 Reaction with H_2 : 1.12.8.1.2
 DyH_2
 Formation: 1.12.4.1
 DyMn_2
 Reaction with H_2 : 1.12.8.1.2
 DyNi_2
 Reaction with H_2 : 1.12.8.1.2
 DyRu_2
 Reaction with H_2 : 1.12.8.1.2
 Er
 Reaction with 1-hexyne: 1.10.5.3
 Er^*Co_2
 ErFe_2
 Reaction with H_2 : 1.12.8.1.2
 ErH_2
 Formation: 1.12.4.1
 ErMn_2
 Reaction with H_2 : 1.12.8.1.2
 ErNi_2
 Reaction with H_2 : 1.12.8.1.2
 ErRu_2
 Reaction with H_2 : 1.12.8.1.2
 EuNi_2
 Reaction with H_2 : 1.12.8.1.2
 EuNi_3
 Reaction with H_2 : 1.12.8.1.1
 EuRh_2
 Reaction with H_2 : 1.12.8.1.2
 F^*Cs
 F^*D
 FGe^*CH_3
 $\text{FGe}^*\text{C}_2\text{H}_7$
 $\text{FGe}^*\text{C}_4\text{H}_{11}$
 FH
 HF
 Formation of atomic hydrogen by reaction with Nb: 1.12.6
 Protonation of F_2NH in AsF_5 : 1.5.3.1.2

FH *cont.*

Protonation of amines: 1.5.3.1.2

Reactions with alkyldichlorophosphines:
1.5.3.2.3Reaction with $(\text{CH}_3)_3\text{NBH}_3$: 1.5.3.1.3Reaction with $(\text{Cl}_3\text{C})_2\text{PClNH}$: 1.5.3.1.3Reaction with SiO or SiO-GeO mix-
tures: 1.6.3.2.1**FNP*** $\text{C}_2\text{H}_2\text{Cl}_7$ **FOP*** C_6H_6 **FP*** Br_2 **FP*** Cl_2 **FSi*** C_6H_{15} **FSn*** C_4H_{11} **FSn*** C_8H_{19} **FSn*** $\text{C}_{12}\text{H}_{11}$ **F***Ca**F₂Ge**GeF₂Insertion into substrate-hydrogen
bonds: 1.6.4.3.1**F₂Ge***CH₄**F₂Ge*** C_2H_6 **F₂Ge*** C_6H_6 **F₂GeSi*** C_3H_{10} **F₂GeSn*** C_6H_{16} **F₂Ge₂*** C_6H_{16} **F₂HK**KHF₂Reaction with $(\text{CH}_3)_2\text{NPF}_2$: 1.5.3.2.3Reaction with PF₃: 1.5.3.2.3Reaction with CF_3PF_2 : 1.5.3.2.3Reaction with $(\text{CF}_3)_2\text{PF}$: 1.5.3.2.3**F₂HN**HNF₂

Formation: 1.5.4.1.2

Hazards in handling: 1.5.3.1.2

Protonation in HF-AsF₅: 1.5.3.1.2**F₂HP**PF₂H

Alcoholysis: 1.5.3.2.3

Formation: 1.5.3.2.3

Reaction with RSH: 1.5.3.2.3

F₂H₂NPPF₂NH₂Reaction with NH₃: 1.5.3.2.3**F₂H₂Na***B**F₂H₃P**PF₂H₃

Formation: 1.5.3.2.3

F₂H₃PSiHF₂SiPH₂

Formation: 1.6.4.2.1

F₂H₅N[NH₄][HF₂]Reaction with R₂Sn: 1.6.3.4.3**F₂H₅N₂P**P(NH₂)₂(F)₂H

Formation: 1.5.3.2.3

F₂IPPF₂IReaction with PH₃ and Hg: 1.5.3.2.3

Reaction with HF and Hg: 1.5.3.2.3

F₂NNF₂

Reaction with thiols: 1.5.4.1.2

F₂N* C_2H_5 **F₂NP*** C_6H_6 **F₂NPSi₂*** C_6H_{18} **F₂O***C**F₂OP*** C_5H_{10} **F₂OP*** C_7H_9 **F₂OP*** C_8H_{11} **F₂O₂Si*** C_4H_{10} **F₂P***Br**F₂P*** C_3H_5 **F₂P*** C_6H_5 **F₂P***Cl**F₂Si**SiF₂

Reaction with HBr: 1.6.3.2.3

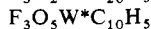
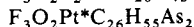
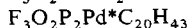
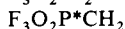
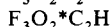
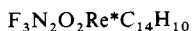
Reaction with PH₃: 1.6.4.2.1Reaction with $(\text{C}_2\text{H}_5)_2\text{SiH}_2$: 1.6.4.2.1**F₂Si*** C_4H_{10} **F₂Si₂*** C_4H_{12} **F₃***B**F₃***CH**F₃***CH₂As**F₃HN**a*B**F₃HSi**SiF₃H

Redistribution: 1.6.4.2.1

F₃H₂PH₂PF₃

Reaction with CsF: 1.5.3.2.3

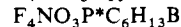
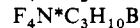
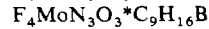
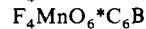
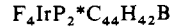
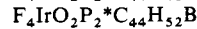
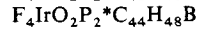
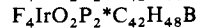
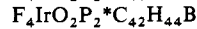
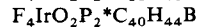
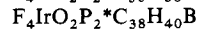
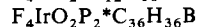
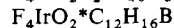
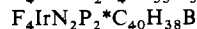
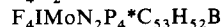
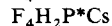
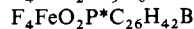
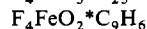
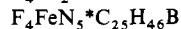
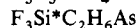
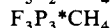
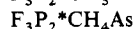
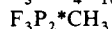
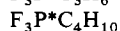
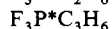
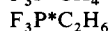
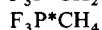
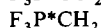
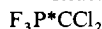
F₃H₂Si*As**F₃I₂***CAs**F₃I₂P***C**F₃MnO₈*** C_6 **F₃N***CCl₂**F₃N***CH₂**F₃NO₈Os₃*** C_{10}H_6 **F₃NO₉Os₃*** C_{11}H_4 **F₃NO₁₀Os₃*** C_{12}H_2 **F₃NO₁₀Os₃*** C_{12}H_4



Protonation in acid: 1.5.3.2.2, 1.5.3.2.3

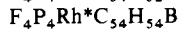
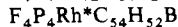
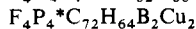
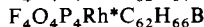
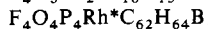
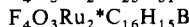
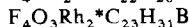
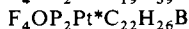
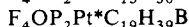
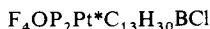
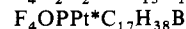
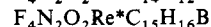
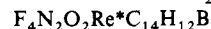
Reaction with Co: 1.10.2

Reaction with $\text{K}[\text{HF}_2]$: 1.5.3.2.3



Dissociation to NF_2 radicals: 1.5.4.1.2

Reaction with B_2H_6 : 1.5.4.1.2



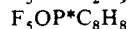
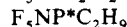
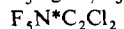
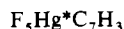
Formation: 1.5.3.2.3



Formation: 1.5.4.2.3

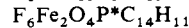
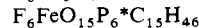
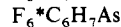
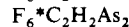
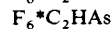
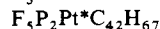


Formation: 1.6.4.2.1



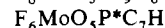
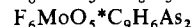
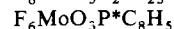
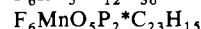
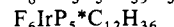
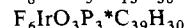
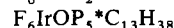
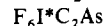
Reaction with $(\text{CH}_3)_3\text{SiH}$: 1.5.4.2.3

Reaction with $(\text{CH}_3)_3\text{SnH}$: 1.5.4.2.3



Reaction with $\text{Co}_3(\text{CO})_9\text{CC}(\text{CH}_3)=\text{C}^*$

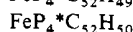
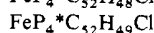
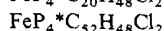
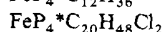
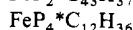
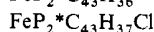
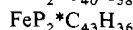
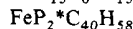
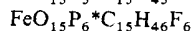
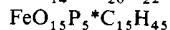
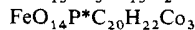
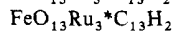
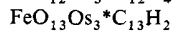
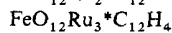
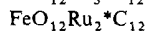
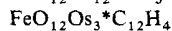
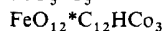
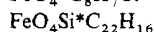
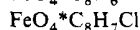
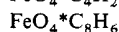
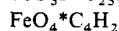
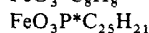
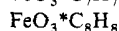
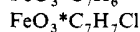
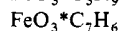
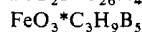
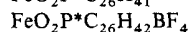
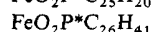
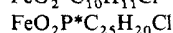
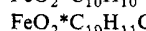
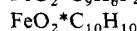
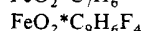
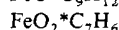
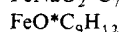
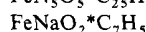
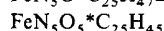
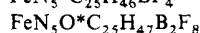
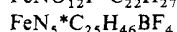
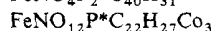
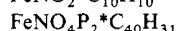
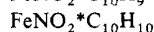
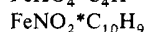
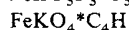
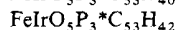
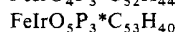
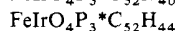
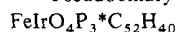
H_2 : 1.6.3.1.3



- $F_6MoO_5PO_5 \cdot C_9H_6As$
 $F_6MoO_5P_2 \cdot C_9H_6$
 $F_6MoP_4 \cdot C_{24}H_{52}$
 $F_6NO_3PRe \cdot C_7H_5$
 $F_6NP_2Pt \cdot C_{39}H_{31}$
 $F_6NSn \cdot C_6H_9$
 $F_6N_2P \cdot C_6H_5$
 $F_6N_2P \cdot C_7H_7$
 $F_6N_2PW \cdot C_{11}H_{12}$
 $F_6N_2PW \cdot C_{12}H_{15}$
 $F_6N_4OOSp \cdot C_{25}H_{16}Cl$
 $F_6N_4OOSp \cdot C_{25}H_{17}$
 $F_6N_4OPRu \cdot C_{21}H_{17}$
 $F_6OPRh_3 \cdot C_{30}H_{48}$
 $F_6OP_5Pt_2 \cdot C_{51}H_{45}$
 $F_6O_3PRh_2 \cdot C_{20}H_{33}$
 $F_6O_5 \cdot C_9H_6As_2Cr$
 $F_6O_5P \cdot C_7HCr$
 $F_6O_5P_2 \cdot C_9H_6Cr$
 $F_6O_6PW_2 \cdot C_{16}H_{11}$
 $F_6O_6P_3Pt_6 \cdot C_{58}H_{47}$
 $F_6O_9Os_3P_2S \cdot C_{21}H_{22}$
 $F_6O_9P \cdot C_{13}H_6Co_3$
 $F_6O_{12}Os_3P \cdot C_{12}H$
 $F_6P \cdot C_2H$
 $F_6PO_5 \cdot C_9H_6AsCr$
 $F_6PRh \cdot C_{11}H_{14}$
 $F_6P_2 \cdot C_2$
 $F_6P_2 \cdot C_2H_2$
 $F_6P_2 \cdot C_4H_6$
 $F_6P_2Ru \cdot C_{30}H_{36}$
 $F_6P_3 \cdot C_{11}H_{24}Co$
 $F_6P_3 \cdot C_{14}H_{23}Co_2$
 $F_6P_3 \cdot C_{16}H_{34}Co$
 $F_6P_3Ir \cdot C_{34}H_{38}$
 $F_6P_4Pt_2S \cdot C_{51}H_{49}$
 $F_6P_4Rh \cdot C_{26}H_{24}$
 $F_6P_5Pt_2 \cdot C_{50}H_{45}Cl_2$
 $F_6P_5Pt_2 \cdot C_{54}H_{54}Cl$
 $F_6P_5Pt_2 \cdot C_{54}H_{55}$
 $F_6P_5W \cdot C_{52}H_{57}$
 $F_7KP \cdot CH$
 $F_7N_2O_2Re \cdot C_{14}H_9B$
 $F_7N_2P \cdot C_6H_4$
 $F_7N_2PW \cdot C_{11}H_{11}$
 $F_7P \cdot C_2$
 $F_8FeN_5O \cdot C_{23}H_{47}B_2$
 $F_8H_2N \cdot As_6$
 $F_8OP \cdot C_9H_7$
 $F_8O_2Pt_2 \cdot C_{32}H_{30}$
 $F_8P_3 \cdot C_{14}H_{32}B_2Co$
 $F_9 \cdot C_3As$
 $F_9 \cdot C_3Bi$
 $F_9IrN_4O_9S_3 \cdot C_{27}H_{16}$
 $F_9KP \cdot C_2H$
 $F_9P \cdot C_3$
 $F_9P_3 \cdot C_3H_2$
 $F_9P_3 \cdot C_8H_{12}Cr$
 $F_9Sb \cdot C_3$
 $F_{10}Zn \cdot C_{12}$
 $F_{12} \cdot C_4As_2$
 $F_{12}FeH_2P_4$
 $H_2Fe(PF_3)_4$
 Formation: 1.10.2, 1.10.3.2
 $F_{12}Fe_2O_6P_2 \cdot C_{10}H_2$
 $F_{12}HP_4 \cdot Co$
 $F_{12}HP_4Rh$
 $HRh(PF_3)_4$
 Formation by protonation of a metal anion: 1.10.3.2
 $F_{12}H_2OsP_4$
 $H_2Os(PF_3)_4$
 Formation: 1.10.3.2
 $F_{12}H_2P_4Ru$
 $H_2Ru(PF_3)_4$
 Formation: 1.10.3.2
 $F_{12}IrN_4P_3 \cdot C_{42}H_{32}$
 $F_{12}KP_4Rh$
 $K[Rh(PF_3)_4]$
 Protonation at metal: 1.10.6.2.1
 $F_{12}MoP_5 \cdot C_{24}H_{53}$
 $F_{12}O_3Pt_2 \cdot C_{32}H_{31}B$
 $F_{12}P_4 \cdot C_4$
 $F_{15}HP_5Re$
 $HRe(PF_3)_5$
 Formation: 1.10.3.2
 $F_{20} \cdot C_{24}Cu_4$
 $F_{20}Na_2Zn_2 \cdot C_{24}H_2$
Fe
 Catalysis of CO reaction with H_2 : 1.6.6.1
 Catalyst for reaction of H_2 with Mg: 1.8.3.2
 Industrial reduction of nitro compounds: 1.5.6.1
 Oxidative addition of CH_4 : 1.10.5.3
 Reaction with H_2 and $o-C_6H_4[(C_2H_5)_2]_2$: 1.10.2
 $Fe \cdot Br_3$
 $Fe \cdot C_{10}H_{10}$
 $Fe \cdot Cl_2$
 $Fe \cdot Cr$
 $FeH_2P_4 \cdot F_{12}$

FeH₂TiTiFeH₂

Pseudobinary metallic hydride: 1.12.1

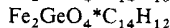
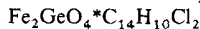
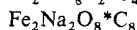
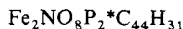
**FeTi**

TiFe

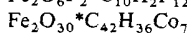
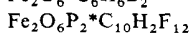
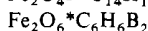
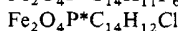
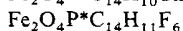
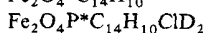
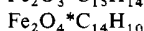
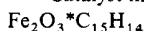
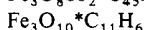
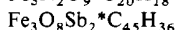
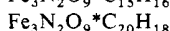
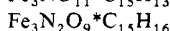
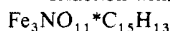
Hydrides: 1.12.8.1.3

Reaction with H₂: 1.12.8.1.3

Disproportionation: 1.12.8.1.2

Reaction with H₂: 1.12.8.1.2Reaction with H₂: 1.12.8.1.2Reaction with H₂: 1.12.8.1.2Reaction with H₂: 1.12.8.1.2

Catalyst in hydride formation: 1.12.8.1.3

Reaction with H₂: 1.12.8.1.2Reaction with H₂: 1.12.8.1.2Reaction with H₂: 1.12.8.1.2Reaction with H₂: 1.12.8.1.2

- $\text{Fe}_3\text{O}_{11} \cdot \text{C}_{12}\text{H}_4$
 $\text{Fe}_3\text{O}_{12} \cdot \text{C}_{12}$
 $\text{Fe}_4\text{NO}_{12} \cdot \text{C}_{12}\text{H}$
 $\text{Fe}_4\text{NO}_{13} \cdot \text{C}_{18}\text{H}_7$
 $\text{Fe}_4\text{N}_2\text{O}_{12} \cdot \text{C}_{20}\text{H}_{20}$
 $\text{Fe}_4\text{O}_{12} \cdot \text{C}_{12}\text{H}_3\text{B}$
 $\text{Fe}_5 \cdot \text{Ce}$
 $\text{Fe}_5\text{NO}_{14} \cdot \text{C}_{14}\text{H}$
 $\text{Fe}_5\text{N}_2\text{O}_{12} \cdot \text{C}_{20}\text{H}_{20}$
 $\text{Fe}_5\text{N}_6\text{O}_{13} \cdot \text{C}_{43}\text{H}_{30}$
 $\text{Fe}_5\text{O}_{12} \cdot \text{C}_{13}\text{H}_2$
 $\text{Ga} \cdot \text{C}_2\text{H}_{10}\text{B}$
 $\text{Ga} \cdot \text{C}_3\text{H}_9$
 $\text{Ga} \cdot \text{Cl}_3$
 $\text{GaH} \cdot \text{Cl}_2$
 $\text{GaH}_4 \cdot \text{Ag}$
 GaH_4Li
 LiGaH_4
 Formation: 1.7.4.3
 $\text{GaH}_9 \cdot \text{B}_2$
 $\text{GaH}_{12} \cdot \text{Al}_3$
 $\text{GaH}_{12} \cdot \text{B}_3$
 $\text{GaN} \cdot \text{C}_3\text{H}_{15}\text{B}$
GaP
 Hydrolysis in aq acid: 1.5.3.2.1
 $\text{Ga}_2 \cdot \text{Br}_6$
 $\text{Ga}_2 \cdot \text{Cl}_6$
 $\text{Ga}_3\text{H}_{12}\text{Ti}$
 $\text{Ti}(\text{GaH}_4)_3$
 Formation: 1.7.5.2
 $\text{Gd} \cdot \text{C}_{15}\text{H}_{15}$
 $\text{Gd} \cdot \text{Co}_2$
 $\text{Gd} \cdot \text{Co}_5$
 $\text{Gd} \cdot \text{Fe}_2$
GdH₂
 Disproportionation of GdFe_2 : 1.12.8.1.2
 Formation: 1.12.4.1
GdMn₂
 Reaction with H_2 : 1.12.8.1.2
GdNi₂
 Reaction with H_2 : 1.12.8.1.1, 1.12.8.1.2
GdRh₂
 Reaction with H_2 : 1.12.8.1.2
GdRu₂
 Reaction with H_2 : 1.12.8.1.2
Ge
 Catalyst for reaction of H_2 with Mg:
 1.8.3.2
 Reaction with H_2 : 1.6.2.3
 Reaction with HBr in presence of Cu:
 1.6.2.3
 Reaction with HCl : 1.6.2.3
 Reaction with $(\text{CH}_3)_3\text{SiH}$: 1.6.2.3
 $\text{Ge} \cdot \text{As}_2\text{Ca}_4$
 $\text{Ge} \cdot \text{CH}_3\text{Br}_3$
 $\text{Ge} \cdot \text{CH}_3\text{Cl}_3$
 $\text{Ge} \cdot \text{CH}_4\text{F}_2$
 $\text{Ge} \cdot \text{CH}_5\text{F}$
 $\text{Ge} \cdot \text{CH}_6$
 $\text{Ge} \cdot \text{CH}_7\text{As}$
 $\text{Ge} \cdot \text{C}_2\text{H}_5\text{Cl}_3$
 $\text{Ge} \cdot \text{C}_2\text{H}_6\text{Cl}_2$
 $\text{Ge} \cdot \text{C}_2\text{H}_6\text{F}_2$
 $\text{Ge} \cdot \text{C}_2\text{H}_7\text{Cl}$
 $\text{Ge} \cdot \text{C}_2\text{H}_7\text{F}$
 $\text{Ge} \cdot \text{C}_2\text{H}_8$
 $\text{Ge} \cdot \text{C}_3\text{H}_9\text{Br}$
 $\text{Ge} \cdot \text{C}_3\text{H}_9\text{Cl}$
 $\text{Ge} \cdot \text{C}_3\text{H}_{10}$
 $\text{Ge} \cdot \text{C}_3\text{H}_{11}\text{As}$
 $\text{Ge} \cdot \text{C}_4\text{H}_{10}$
 $\text{Ge} \cdot \text{C}_4\text{H}_{10}\text{Cl}_2$
 $\text{Ge} \cdot \text{C}_4\text{H}_{11}\text{Cl}$
 $\text{Ge} \cdot \text{C}_4\text{H}_{11}\text{Cl}_3\text{O}$
 $\text{Ge} \cdot \text{C}_4\text{H}_{11}\text{F}$
 $\text{Ge} \cdot \text{C}_4\text{H}_{12}$
 $\text{Ge} \cdot \text{C}_4\text{H}_{13}\text{As}$
 $\text{Ge} \cdot \text{C}_5\text{H}_8$
 $\text{Ge} \cdot \text{C}_5\text{H}_{11}\text{Br}_3$
 $\text{Ge} \cdot \text{C}_5\text{H}_{14}$
 $\text{Ge} \cdot \text{C}_6\text{H}_5\text{Cl}_3$
 $\text{Ge} \cdot \text{C}_6\text{H}_6\text{F}_2$
 $\text{Ge} \cdot \text{C}_6\text{H}_8$
 $\text{Ge} \cdot \text{C}_6\text{H}_{15}\text{Br}$
 $\text{Ge} \cdot \text{C}_6\text{H}_{15}\text{Cl}$
 $\text{Ge} \cdot \text{C}_6\text{H}_{16}$
 $\text{Ge} \cdot \text{C}_7\text{H}_{16}$
 $\text{Ge} \cdot \text{C}_9\text{H}_{15}\text{As}$
 $\text{Ge} \cdot \text{C}_9\text{H}_{22}$
 $\text{Ge} \cdot \text{C}_{12}\text{H}_{10}\text{Br}_2$
 $\text{Ge} \cdot \text{C}_{12}\text{H}_{10}\text{Cl}_2$
 $\text{Ge} \cdot \text{C}_{12}\text{H}_{11}\text{Cl}$
 $\text{Ge} \cdot \text{C}_{12}\text{H}_{12}$
 $\text{Ge} \cdot \text{C}_{12}\text{H}_{28}$
 $\text{Ge} \cdot \text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{Ge} \cdot \text{C}_{18}\text{H}_{15}\text{D}$
 $\text{Ge} \cdot \text{C}_{18}\text{H}_{16}$
 $\text{Ge} \cdot \text{C}_{18}\text{H}_{34}$
 $\text{Ge} \cdot \text{C}_{20}\text{H}_{34}$
 $\text{Ge} \cdot \text{C}_{21}\text{H}_{22}$
 $\text{Ge} \cdot \text{Ca}$
 $\text{Ge} \cdot \text{Cl}_2$
 $\text{Ge} \cdot \text{Cl}_4$
 $\text{Ge} \cdot \text{D}_4$

- Ge*F₂**
GeH
 (GeH)_x
 Formation: 1.6.3.3.1, 1.6.3.3.2
GeH*Br₃
GeH*Cl₃
GeH₃
 Reduction by Li[AlH₄]: 1.6.5.3.1
GeH₂
 (GeH₂)_x
 Formation: 1.6.2.3, 1.6.3.3.2, 1.6.5.3.1,
 1.6.5.3.2
 Reaction with HCl: 1.6.3.3.3
GeH₂*Br₂
GeH₂*Cl₂
GeH₂I₂
 Reduction by Li[AlH₄]: 1.6.5.3.1
GeH₂O
 (GeH₂O)_n
 Formation: 1.6.4.3.3
GeH₂O₂
 Ge(OH)₂
 Reaction with aq HBr: 1.6.3.3.1
GeH₃*Br
GeH₃*Cl
GeH₃*D
GeH₃D
 Formation: 1.6.7.1.3
GeH₃I
 Reduction by Li[AlH₄]: 1.6.5.3.1
GeH₃K
 K[GeH₃]
 Reaction with hydrogen halides:
 1.6.3.3.3
GeH₃Li
 Li[GeH₃]
 Reaction with hydrogen halides:
 1.6.3.3.3
GeH₃Na
 Na[GeH₃]
 Electrolysis in liq NH₃: 1.6.3.3.2
 Reactions with hydrogen halides:
 1.6.3.3.2
 Reaction with NH₄Br in liq NH₃:
 1.6.3.3.2
GeH₄
 Exchange with basic D₂O: 1.6.7.2.3
 Formation: 1.6.3.3.1, 1.6.3.3.2, 1.6.3.3.3,
 1.6.4.3.1, 1.6.4.3.2, 1.6.4.3.3, 1.6.5.3.1,
 1.6.5.3.2, 1.6.7.1.3
 Hg-sensitized photolysis: 1.6.4.3.3
 Industrial synthesis: 1.6.6.3
 Pyrolysis in presence of SiH₄: 1.6.4.2.3
 Reaction in silent electric discharge:
 1.6.4.3.3
 Reaction with AsH₃ in silent electric
 discharge: 1.5.4.3
 Reaction with (C₂H₅)₃GeLi: 1.6.3.3.3
 Reaction with PH₃ or AsH₃ in silent
 electric discharge: 1.6.4.3.3
 Reaction with SiH₄ in silent electric
 discharge: 1.6.4.2.3
 Reaction with metal germanides:
 1.6.3.3.3
 Thermolysis: 1.6.4.3.3
 Thermolysis in presence of SiH₄:
 1.6.4.3.3
GeH₅*As
GeH₅P
H₃GePH₂
 Decomposition to PH₃: 1.5.4.2.4
 Formation: 1.5.3.2.1, 1.6.3.3.1, 1.6.4.3.3
 Formation from PH₃ and GeH₄ in si-
 lent electric discharge: 1.5.4.2.2
GeH₆K*B
GeH₆Si
H₃GeSiH₃
 Formation: 1.6.3.3.1, 1.6.4.2.3, 1.6.4.3.3,
 1.6.5.3.1
GeH₆Sn
H₃GeSnH₃
 Formation: 1.6.4.3.2
GeH₆Si₂
Si₂GeH₈
 Formation: 1.6.3.2.1, 1.6.4.2.3, 1.6.4.3.3
GeH₁₀Si₃
i-Si₃GeH₁₀
 Formation: 1.6.4.2.3, 1.6.4.3.3
n-Si₃GeH₁₀
 Formation: 1.6.4.2.3, 1.6.4.3.3
GeH₁₂Si₄
(SiH₃)₂SiHSiH₂GeH₃
 Formation: 1.6.4.3.3
GeK*C₃H₁₂B
GeK*C₆H₁₅
GeK*C₁₈H₁₅
GeK*C₂₁H₂₁
GeLi*C₆H₁₅
GeLi*C₁₈H₁₅
GeLi*C₂₁H₂₁
GeMg*C₆H₁₅Cl
GeMg*C₉H₂₁Cl
GeMg*C₁₈H₁₅Cl
GeMg*C₁₈H₃₃Cl

GeMg₂Mg₂Ge[NH₄]Br protonation of Mg₂Ge in liqNH₃: 1.6.3.3.2

Protonation by acids: 1.6.3.3.1

Reaction with D₂O-DCl: 1.6.7.1.3

Reaction with protonic acids: 1.6.6.3

GeMg₄SiMg₄SiGe

Hydrolysis by 10% HF: 1.6.3.3.1

GeMg₂₀Si₉Mg₂₀Si₉Ge

Hydrolysis: 1.6.3.2.1

GeN*C₅H₁₅GeN₃*C₃H₉**GeNa**(NaGe)_xProtonation by [NH₄]Br in liq NH₃:

1.6.3.3.2

Reaction with aq acid: 1.6.3.3.1

GeNa*C₆H₁₅GeNa*C₁₈H₁₅GeNa*C₂₁H₂₁**GeNa₂O₃**Na₂GeO₃Reduction in basic K[BH₄]: 1.6.5.3.2GeNiP₃*C₆₆H₅₅DGeNiP₃*C₆₆H₅₆**GeO**

Reaction with HCl: 1.6.3.3.3

GeO*C₄H₁₁Cl₃GeO*C₁₈H₁₆**GeO₂**Reaction with Li[AlH₄]: 1.6.5.3.2Reaction with (i-C₄H₉)₂AlH: 1.6.4.3.2GeO₂*CH₄GeO₂*C₁₆H₃₄**GeO₂Si**

SiO-GeO

Hydrolysis: 1.6.3.3.1

Reaction with dil HF: 1.6.3.2.1

GeO₄*C₁₄H₁₀Cl₂Fe₂GeO₄*C₁₄H₁₂Fe₂GeO₃Sn*C₈H₁₂GeP*CH₇GeP*C₂H₉GeP*C₉H₂₁GeP*C₉H₂₂ClGeP*C₉H₂₃GeP*C₁₀H₂₅GeP*C₁₈H₂₅GeP*C₃₆H₃₀AuGeP*C₃₆H₃₁AuGeP₂*CH₈GeP₂*C₂H₁₀GeP₂*C₄H₁₄GeP₂Pd*C₄₈H₆₀GeP₂Pt*CH₄₄Cl₂GeS*C₂H₆GeSi*C₃H₁₀F₂GeSi*C₆H₁₈GeSi*C₁₃H₃₂GeSi*C₂₀H₃₀GeSi*Cl₆GeSi₂*C₆H₂₀GeSn*C₆H₁₆F₂GeTi*C₂₈H₂₅ClGe₂*C₂H₁₀Ge₂*C₅H₁₆Ge₂*C₆H₁₆F₂Ge₂*C₆H₁₈Ge₂*C₁₂H₂₈Cl₂Ge₂*C₁₂H₃₀Ge₂*C₁₂H₃₀CdGe₂*C₁₃H₃₂Ge₂*D₆**Ge₂H₈I**H₃GeGeH₂IReduction by Li[AlH₄]: 1.6.5.3.1**Ge₂H₆**Disproportionation in liq. NH₃: 1.6.3.3.2

Formation: 1.6.3.3.1, 1.6.4.3.3, 1.6.5.3.1,

1.6.5.3.2

Pyrolysis in presence of Si₂H₆: 1.6.4.2.3,

1.6.4.3.3

Pyrolysis in presence of Si₃H₈: 1.6.4.2.3,

1.6.4.3.3

X-Irradiation in presence of C₂H₆:

1.6.4.3.3

Ge₂H₆O(H₃Ge)₂O

Disproportionation: 1.6.4.3.3

Ge₂H₇P(H₃Ge)₂PHFormation from GeH₄-PH₃: 1.5.4.2.2**Ge₂H₈Si**SiGe₂H₈

Formation: 1.6.3.2.3, 1.6.3.3.1

Ge₂H₁₀Si₂n-Si₂Ge₂H₁₀

Formation: 1.6.3.3.1

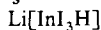
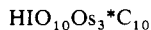
Ge₂H₁₂Si₃n-Si₃Ge₂H₁₂

Formation: 1.6.3.3.1

- $\text{Ge}_2\text{N}^*\text{C}_{24}\text{H}_{55}$
 $\text{Ge}_2\text{NSn}^*\text{C}_{42}\text{H}_{45}$
 $\text{Ge}_2\text{O}^*\text{C}_{36}\text{H}_{30}$
 $\text{Ge}_2\text{P}_2\text{Pd}^*\text{C}_{48}\text{H}_{60}$
 $\text{Ge}_2\text{P}_2\text{Pt}^*\text{C}_{33}\text{H}_{54}$
 $\text{Ge}_2\text{P}_2\text{Pt}^*\text{C}_{48}\text{H}_{60}$
 $\text{Ge}_2\text{P}_2\text{Pt}^*\text{C}_{54}\text{H}_{72}$
 $\text{Ge}_2\text{S}_2^*\text{C}_4\text{H}_{12}$
 $\text{Ge}_3^*\text{C}_2\text{H}_{12}$
 $\text{Ge}_3^*\text{C}_7\text{H}_{22}$
 $\text{Ge}_3^*\text{C}_9\text{H}_{27}\text{Bi}$
 $\text{Ge}_3^*\text{C}_{18}\text{H}_{45}\text{Bi}$
 Ge_3^*D_8
 Ge_3H_8
 Formation: 1.6.3.3.1, 1.6.4.3.3, 1.6.5.3.2
 Formation from GeH_4 in silent electric discharge: 1.5.4.2.2
 Reaction with $\text{H}(\text{SiH}_3)_2\text{SiSiH}_3$: 1.6.4.3.3
 $\text{Ge}_3\text{H}_9^*\text{As}$
 $\text{Ge}_3\text{H}_9\text{P}$
 $(\text{H}_3\text{Ge})_3\text{P}$
 Decomposition to PH_3 : 1.5.4.2.4
 Disproportionation: 1.6.4.3.3
 Reaction with H_2S : 1.5.3.2.3
 $\text{Ge}_3\text{H}_9\text{Sb}$
 $(\text{H}_3\text{Ge})_3\text{Sb}$
 Cleavage by HCl : 1.5.3.4
 $\text{Ge}_3\text{H}_{10}\text{Si}$
 n- $\text{SiGe}_3\text{H}_{10}$
 Formation: 1.6.3.3.1
 Ge_3N_2
 Reaction with H_2 : 1.5.2.1.2
 $\text{Ge}_3\text{Sb}^*\text{C}_{18}\text{H}_{45}$
 $\text{Ge}_3\text{Ti}^*\text{C}_{18}\text{H}_{45}$
 $\text{Ge}_4^*\text{C}_{54}\text{H}_{46}$
 Ge_4H_{10}
 $\text{H}_3\text{Ge}(\text{GeH}_2)_2\text{GeH}_3$
 Formation: 1.6.3.3.1
 $\text{Ge}_4\text{Li}^*\text{C}_{54}\text{H}_{45}$
 Ge_5H_{12}
 Formation: 1.6.3.3.1, 1.6.4.3.3
 $\text{Ge}_5\text{H}_{14}\text{P}_2$
 $[(\text{H}_3\text{Ge})_2\text{P}]_2\text{GeH}_2$
 Formation: 1.6.4.3.3
 $\text{Ge}_5\text{H}_{14}\text{Si}$
 n- $\text{H}_3\text{Si}(\text{GeH}_2)_4\text{GeH}_3$
 Formation: 1.6.3.2.1
 $\text{Ge}_6\text{P}_4^*\text{C}_{12}\text{H}_{36}$
 $\text{Ge}_6\text{P}_4^*\text{C}_{24}\text{H}_{60}$
H
 Reaction with ICN : 1.6.2.1.1
 Reaction with P_4O_{10} : 1.5.2.2
 Reaction with Pb film: 1.6.2.5
 Reaction with SiH_4 : 1.6.2.2
 Reaction with Sn , SnCl_2 or SnCl_4 : 1.6.2.4
 Reaction with C : 1.6.2.1.1
 Reaction with red phosphorus: 1.5.2.2
H*Ag
H*Ag₂Ca
HAsF₆*C₂
H*BCl₂
H*BF₄
H*Br
H*BrCd
H*Br₃Ge
H*C
H*Cl
H*Cl₂Ga
H*Cl₃Ge
HCl₇NP*C₂
HCoO₄*C₄
HCoO₁₃Ru₃*C₁₃
HCo₃FeO₁₂*C₁₂
HCo₃O₁₂Os*C₁₂
HCo₆KO₁₅*C₁₅
H*Cr
HCrF₆O₅P*C₇
HCr₂KO₁₀*C₁₀
H*Cs
H*C_u
H*F
HF₃*C
HF₃O₂*C₂
HF₄N*C₂
HF₅*C₆
HF₆MoO₅P*C₇
HF₆O₁₂Os₃P*C₁₂
HF₆P*C₂
HF₇KP*C
HF₉KP*C₂
HFeKO₄*C₄
HFe₄NO₁₂*C₁₂
HFe₅NO₁₄*C₁₄
H*Ge
HHg
 HgH
 From photosensitized decomposition of alkanes: 1.9.5.2
HI
 Protonation of amines: 1.5.3.1.2
 Reaction with CF_3AsI_2 and Hg : 1.5.3.3.3

HI *cont.*

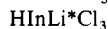
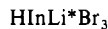
- Reaction with $(\text{CF}_3)_2\text{AsI}$ and Hg: 1.5.3.3.3
- Reaction with $(\text{CF}_3)_4\text{P}_2$: 1.5.3.2.3
- Reaction with amides: 1.5.3.1.3
- Reaction with iodophosphines and Hg: 1.5.3.2.3



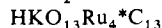
- Formation: 1.7.4.4



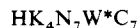
- Formation: 1.10.3.2

**HK**

- Addition to triorganylboranes: 1.7.4.1.3
- Formation: 1.8.2.2
- Reaction with Si₂H₆: 1.6.4.2.3
- Reaction with CO: 1.6.4.1.2
- Reaction with CO₂: 1.6.4.1.2
- Reduction of $(\text{s-C}_4\text{H}_9)_2\text{Zn}$ to K₂[ZnH₄]: 1.9.4.1
- Reduction of C₆H₅CH₂Cl: 1.6.4.1.1
- Reduction of halogermanes: 1.6.4.3.1



- Reaction with protonic acids: 1.5.3.1.3

**HLi**

- Formation: 1.8.2, 1.8.2.1
- Reaction with CH₃PCl₂, (CH₃)₂PCl and C₆H₅PCl₂: 1.5.4.2.1
- Reaction with SiCl₄ and H₂ in LiCl-K* Cl eutectic: 1.6.6.2
- Reaction with CO₂: 1.6.4.1.2
- Reduction of GeCl₄: 1.6.4.3.1
- Reduction of PBr₃: 1.5.4.2.1
- Reduction of (C₂H₅)₂Si(OC₂H₅)₂: 1.6.4.2.2
- Reduction of CH₂=CHCH₂SiCl₃: 1.6.4.2.1
- Reduction of C₆H₅SiCl₃: 1.6.6.2
- Reduction of CH₃CHClSiCl₃: 1.6.4.2.1

- Reduction of ZnBr₂ to ZnH₂: 1.9.4.1

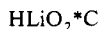
- Reduction of C₆H₅CH₂Cl: 1.6.4.1.1

- Reduction of alkoxyasilanes: 1.6.4.2.2

- Reduction of halogermanes: 1.6.4.3.1

- Reduction of halosilanes: 1.6.4.2.1

- Theoretical stability calculations: 1.12.1



- Formation: 1.5.4.1.3

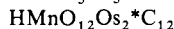
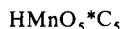
- Reaction with protonic acids: 1.5.3.1.3



- Formation: 1.5.4.2.4

HMn

- Formation: 1.12.7

**HMnO**

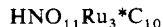
- Formation: 1.12.7



- Reaction with protonic acids: 1.5.3.1.3

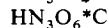


- Reduction to [NH₃OH]⁺: 1.5.3.1.1



- Formation: 1.5.3.1.3

- Thermolysis to NH₃: 1.5.4.1.3

**HNa**

- Formation: 1.8.2.2

- Reaction with B₁₀H₁₂CN(CH₃)₃: 1.6.4.1.3

- Reaction with (C₂H₅)₂SiF₂: 1.6.4.2.1

- Reaction with SiCl₄ and H₂ in LiCl-K* Cl eutectic: 1.6.6.2

- Reaction with (C₆H₅)₃SiCH₂C₆H₅: 1.6.4.2.3

- Reaction with CO₂: 1.6.4.1.2

- Reduction of (C₂H₅O)₂SiF₂: 1.6.4.2.1

- Reduction of (OC₂H₅)₂SiCl₂: 1.6.4.2.2

- Reduction of (C₆H₅)₃SiCl: 1.6.4.2.1

- Reduction of SiCl₄: 1.6.4.2.1

- Reduction of ZnCl_2 to ZnH_2 : 1.9.4.1
 Reduction of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$: 1.6.4.1.1
 Reduction of $\text{C}_6\text{H}_5\text{I}$: 1.6.4.1.1
 Reduction of halogermanes: 1.6.4.3.1
- HNa*BF₃**
HNaO
 NaOH
 Preparation of UH_3 : 1.12.4.2
 Reaction with H_2 and carbon: 1.8.2.2
- HNaO₂*C**
HNaO₃*C
HNa₂O₅V*C₅
HNa₂PS₃
 $\text{Na}_2[\text{HP}(\text{S})\text{S}_2]$
 Conversion to PH_3 : 1.5.3.2.3
- HNb**
NbH
 Formation: 1.12.6
- HNi**
NiH
 Formation: 1.12.7
- HO₄*Cl**
HO₅Re*C₅
HO₆V*C₆
- HP**
 $(\text{PH})_n$
 Formation: 1.5.3.2.3, 1.5.4.2.1, 1.5.4.2.4
 Formation from $\text{CF}_3\text{As}(\text{PH}_2)_2$ redistribution: 1.5.4.3
- HP*C**
HP*D₂
HP*F₂
HP*F₅
HP*F₆
HP₄*CoF₁₂
HP₄Rh*F₁₂
HP₅Re*F₁₅
- HPd**
PdH
 Band structure: 1.12.1
 Formation: 1.12.7
- HRb**
RbH
 Formation: 1.8.2.2
 Reaction with N_2 : 1.5.4.1.1
- HRh**
RhH
 Formation: 1.12.7
- HSi*Cl₃**
HSi*F₃
HSi₂*F₅
- HTa**
TaH
 Formation: 1.12.6
- HTc**
TcH
 Formation: 1.12.7
- HTl**
TlH
 Formation: 1.7.5.2
 $(\text{TiH})_x$
 Formation: 1.7.3.2
- HV**
VH
 Formation: 1.12.6
- H₂**
 By-product from ZnH_2 reaction of $(\text{C}^*\text{H}_3)_2\text{NCH}_2\text{CH}_2\text{NHCH}_3$: 1.9.4.1
 Cleavage of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$: 1.6.6.1
 Direct synthesis of alkali-metal hydrides: 1.8.2
 Ion-molecule reactions with group-0 elements: 1.11
 Preparation of hydrides: 1.12.1, 1.12.4.1, 1.12.4.2, 1.12.5, 1.12.6, 1.12.7, 1.12.8.1.1, 1.12.8.1.2, 1.12.8.2.2, 1.12.8.2.4
 Reaction with $(\text{C}_6\text{H}_5)_3\text{As}$ and $(\text{C}_6\text{H}_5)_3\text{Bi}$: 1.6.2.1.2
 Reaction with Be: 1.8.3.1
 Reaction with Ca, Sr, Ba and Ra: 1.8.3
 Reaction with Ca, Sr and Ba: 1.8.3.3
 Reaction with $[\text{CH}_2\text{CHCH}_2\text{Co}(\text{C}^*\text{N})_5]^{3-}$: 1.6.2.1.2
 Reaction with $[\text{C}_6\text{H}_5\text{CH}_2\text{Cr}(\text{H}_2\text{O})_5]^{2+}$: 1.6.2.1.2
 Reaction with $[\text{Fe}_4\text{C}(\text{CO})_{12}]^-$: 1.6.2.1.2
 Reaction with Ge: 1.6.2.3
 Reaction with Ge_3N_2 : 1.5.2.1.2
 Reaction with $\text{C}_6\text{H}_5\text{HgOCOCH}_3$: 1.6.2.1.2
 Reaction with Li: 1.8.2.1
 Reaction with Mg: 1.8.3.2
 Reaction with Na, K, Rb and Cs: 1.8.2.2
 Reaction with C_2H_6 over Ni-Cu catalyst: 1.6.2.1.2
 Reaction with $\{[(\text{C}_6\text{H}_5)_4\text{C}_4]\text{PdCl}_2\}_2$: 1.6.2.1.2
 Reaction with $\text{HOs}(\text{CO})_4\text{CH}_3$: 1.6.2.1.2
 Reaction with $\text{HOs}_3(\text{CO})_{10}(\text{NCHCF}_3)$: 1.5.2.1.2
 Reaction with $[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{PdGe}(\text{C}_6\text{H}_5)_3]_2$: 1.6.2.3

H₂ *cont.*

Reaction with CH₃C₆H₅ over Pt-SiO₂: 1.6.6.1
 Reaction with [(C₂H₅)₃P]₂Pt[Ge(C₆H₅)₃]₂: 1.6.2.3
 Reaction with Pt[Sn(CH₃)₃]₂[P(C₆H₅)₃]₂: 1.6.2.4
 Reaction with CO and [HRu(CO-)₁₀[Si(C₂H₅)₃]₂]⁻: 1.6.2.2
 Reaction with SiO₂ in presence of Al and AlCl₃: 1.6.2.2
 Reaction with SiCl₄: 1.6.2.2
 Reaction with SiCl₄ and Al in AlCl₃: 1.6.6.2
 Reaction with (C₆H₅)₃SiSi(C₆H₅)₃ over Cr: 1.6.2.2
 Reaction with (h⁵-C₅H₅)₂Zr(CO)₂: 1.6.2.1.2
 Reaction with (h⁵-C₅H₅)₂Zr(H)CH₂C₆H₅*H₁₁: 1.6.2.1.2
 Reaction with C₆H₅CH(NC₆H₅): 1.5.2.1.2
 Reaction with C₆H₅NO₂: 1.5.2.1.2
 Reaction with CH₃CO(CH₃O)C₆H₃C*H(CO₂H)NHCOCH₃: 1.6.2.1.2
 Reaction with C₆H₅NO: 1.5.2.1.2
 Reaction with N-nitrosoamine: 1.5.2.1.2
 Reaction with Ca(CN)₂: 1.5.2.1.2
 Reaction with N₂: 1.5.2.1.1
 Reaction with N₂ to form NH₃: 1.5.6.1
 Reaction with CO and n-C₄H₉CH=C*H₂: 1.6.2.1.2
 Reaction with CO to form CH₃OH: 1.6.6.1
 Reaction with [C₂H₅]⁺ in gas phase: 1.6.2.1.2
 Reaction with C₄H₄O in presence of Ni: 1.6.6.1
 Reaction with CO₂ over Ni: 1.6.2.1.2
 Reaction with CO: 1.6.2.1.2
 Reaction with CO and olefins: 1.6.6.1
 Reaction with (CH₃)₂CO: 1.6.2.1.2
 Reaction with CH₃C≡CCH₃: 1.6.2.1.2, 1.6.6.1
 Reaction with CH₂CHCH₂CH₂CH₃: 1.6.6.1
 Reaction with C₆H₆: 1.6.2.1.2
 Reaction with C₆H₅CN: 1.6.2.1.2
 Reaction with H₂ to produce (CH₂OH)₂: 1.6.6.1
 Reaction with alkenes: 1.6.6.1
 Reaction with alkynes: 1.6.6.1
 Reaction with arenes: 1.6.6.1

Reaction with azide: 1.5.2.1.2
 Reaction with carbon at high temperatures: 1.6.2.1.1
 Reaction with carbon atoms from C₃O₂: 1.6.2.1.1
 Reaction with distannanes: 1.6.2.4
 Reaction with esters: 1.6.6.1
 Reaction with imine: 1.5.2.1.2
 Reaction with organic substrates in presence of catalysts: 1.6.2.1.2
 Reaction with oxime: 1.5.2.1.2
 Reaction with selenophosphinic acid: 1.5.2.2
 Reaction with thiophosphinic acid: 1.5.2.2
 Reaction with transition metals: 1.9.1
 Reduce CuI in liq NH₃: 1.9.5.2
 Reduction of (h⁵-C₅H₅)₂Ti(CO)₂: 1.6.2.1.2
 Reduction of C₅H₅N over Pt: 1.5.6.1

H₂*Ac
 H₂*AsD
 H₂AsF₃*C
 H₂As₂F₆*C₂
 H₂*B₁₀D₁₂
 H₂*Ba
 H₂*Be
 H₂*Br₂Ge
 H₂*C₂
 H₂*Ca
 H₂*Cd
 H₂*Ce
 H₂*Cl₂Ge
 H₂*Cl₆Ir
 H₂Cl₇FNP*C₂
 H₂Co₂O₁₂Ru₂*C₁₂
 H₂*Cr
 H₂D₂O₁₂Ru₄*C₁₂
 H₂*Dy
 H₂*Er
 H₂F₃N*C
 H₂F₃NO₁₀Os₃*C₁₂
 H₂F₃O₂P*C
 H₂F₃P*C
 H₂F₆P₂*C₂
 H₂F₉P₃*C₃
 H₂F₁₂Fe₂O₆P₂*C₁₀
 H₂F₂₀Na₂Zn₂*C₂₄
 H₂FeO₄*C₄
 H₂FeO₁₃Os₃*C₁₃
 H₂FeO₁₃Ru₃*C₁₃
 H₂Fe₅O₁₂*C₁₃

- H_2^*Gd
 H_2^*Ge
 H_2Hf
 HfH_2
 Formation: 1.12.5
 H_2Hg
 $(\text{HgH}_2)_n$
 Formation: 1.9.5.2
 H_2Ho
 HoH_2
 Formation: 1.12.4.1
 H_2IN
 NH_2I
 Formation: 1.5.3.1.2
 $\text{H}_2\text{I}_2^*\text{Ge}$
 $\text{H}_2\text{K}^*\text{As}$
 $\text{H}_2\text{K}^*\text{Cu}$
 H_2KN
 H_2NK
 Reaction with protonic acids: 1.5.3.1.3
 H_2KP
 KPH_2
 Protonation to PH_3 : 1.5.3.2.2
 H_2La
 LaH_2
 Disproportionation of LaNi_5 : 1.12.8.1.1
 $\text{H}_2\text{Li}^*\text{Cu}$
 H_2LiN
 LiNH_2
 Reaction with protonic acids: 1.5.3.1.3
 Thermal decomposition to NH_3 :
 1.5.4.1.3
 H_2LiP
 LiPH_2
 Formation from H_3SiPHLi redistribution: 1.5.4.2.4
 Reaction with P_4 : 1.5.4.2.2
 H_2Lu
 LuH_2
 Formation: 1.12.4.1
 H_2Mg
 MgH_2
 Formation: 1.8.3, 1.8.3.2
 Transition between saline and covalent hydrides: 1.12.1
 $\text{H}_3\text{N}^*\text{As}_6\text{F}_8$
 $\text{H}_3\text{N}^*\text{Br}$
 $\text{H}_2\text{N}^*\text{Cl}$
 $\text{H}_3\text{N}^*\text{Cs}$
 $\text{H}_2\text{N}^*\text{Na}$
 $\text{Na}[\text{NH}_2]$
 Reaction with NaNO_3 : 1.5.4.1.3
 Reaction with N_2O : 1.5.4.1.3
 Reaction with protonic acids: 1.5.3.1.3
 $\text{H}_2\text{NP}^*\text{F}_2$
 H_2NRb
 $\text{Rb}[\text{NH}_2]$
 Formation: 1.5.4.1.1
 $\text{H}_2\text{N}_2^*\text{C}$
 $\text{H}_2\text{N}_2\text{O}_2\text{P}_2^*\text{Cl}_4$
 $\text{H}_2\text{N}_2\text{O}_7^*\text{Co}$
 $\text{H}_2\text{Na}^*\text{BF}_2$
 $\text{H}_2\text{NaO}_2\text{P}$
 $\text{NaP}(\text{OH})_2$
 Reactions with alkyl halides: 1.5.3.2.3
 $\text{H}_2\text{Na}_2\text{O}_4\text{P}_2$
 $\text{Na}_2[\text{H}_2\text{P}_2\text{O}_4]$
 Industrial synthesis: 1.5.6.2
 H_2Nb
 NbH_2
 Formation: 1.12.6
 H_2Nd
 NdH_2
 Formation: 1.12.4.1
 H_2O
 Cleavage of group-IVB arsines: 1.5.3.3.3
 Cleavage of group-IV phosphines:
 1.5.3.2.3
 Hydrolysis of PCl_3 to form H_3PO_3 :
 1.5.6.2
 Hydrolysis of C_2H_4 : 1.6.6.1
 Hydrolysis of $\text{CH}_3\text{CH}=\text{CH}_2$: 1.6.6.1
 Hydrolysis of $\text{CH}_3\text{C}\equiv\text{CCH}_3$: 1.6.6.1
 Impurity in H_2 : 1.8.2
 Poison for hydriding reaction: 1.12.8.1.1
 Reaction with $(\text{CH}_3)_3\text{Al}$: 1.6.2.5
 Reaction with Al_4C_3 : 1.6.6.1
 Reaction with $[(\text{CH}_3)_2\text{CHO}]_3\text{B}$:
 1.6.4.1.2
 Reaction with $\text{B}_{10}\text{H}_{13}\text{CN}[\text{Si}(\text{CH}_3)_3]_2$:
 1.5.3.1.3
 Reaction with Be_2C or Al_4C_3 : 1.6.2.5
 Reaction with $(\text{CH}_3)_3\text{GeN}_3$: 1.5.3.1.3
 Reaction with $(\text{C}_6\text{H}_5)_3\text{GeLi}$: 1.6.3.3.3
 Reaction with CH_3Li , $\text{C}_2\text{H}_5\text{Li}$, $i\text{-C}_3\text{H}_7\text{Li}$ or $t\text{-C}_4\text{H}_9\text{Li}$: 1.6.2.5
 Reaction with $n\text{-C}_4\text{H}_9\text{MgBr}$: 1.6.2.5
 Reaction with $\text{C}_{10}\text{H}_7\text{Na}$: 1.6.2.5
 Reaction with $\text{Nd}(\text{C}_5\text{H}_5)_3$: 1.6.2.5
 Reaction with $(\text{CH}_3)_2\text{P}(\text{S})\text{N}[\text{Si}(\text{C}^*\text{H}_3)_3]_2$: 1.5.3.1.3
 Reaction with $(\text{C}_6\text{H}_5)_3\text{PNR}$: 1.5.3.1.3
 Reaction with $(\text{CF}_3)_3\text{P}$, $(\text{CF}_3)_3\text{As}$,
 $(\text{CF}_3)_3\text{Sb}$, $(\text{CF}_3)_3\text{Bi}$: 1.6.2.5

H₂O *cont.*

- Reaction with (CF₃)₄P₂: 1.5.3.2.3
- Reaction with (CH₃)₃SiN₃: 1.5.3.1.3
- Reaction with (CH₃)₂Si: 1.6.3.2.1
- Reaction with (C₂H₅)₃SnB[N(CH₃)₂]₂: 1.6.3.4.1
- Reaction with (C₂H₅)₃SnC₆H₅: 1.6.2.5
- Reaction with [(C₂H₅)₃SnN(CO₂C₂H₅)₂]: 1.5.3.1.3
- Reaction with [(C₆H₅)₃Sn]₂Mg: 1.6.3.4.1
- Reaction with CaH₂, SrH₂, BaH₂: 1.8.3.3
- Reaction with ZnC₂ to form C₂H₂: 1.6.6.1
- Reaction with CH₃ZrCl(C₅H₅-h⁵)₂: 1.6.3.1.3
- Reaction with [CN]⁻, [(CN)₃C]⁻ or [(NO₂)₃C]⁻: 1.6.2.5
- Reaction with carbon atoms: 1.6.2.1.1
- Reaction with elemental boron: 1.7.2
- Reaction with metals to form hydrides: 1.12.4.1

H₂O*C**H₂O***Ge**H₂O₂***C**H₂O₂***Ge**H₂O₂**VV(OH)₂

- Reduction of aq N₂ to N₂H₄: 1.5.3.1.1

H₂O₄Os*C₄**H₂O₄P₂***Ba**H₂O₄Ru***C₄**H₂O₄S****H₂SO₄**

- Electrolyte cathodic charging of Ti: 1.12.5
- Electrolyte for electrodeposition of CrH and CrH₂: 1.11.2.7
- Electrolyte in cathodic charging of Ni: 1.12.7
- Electrolyte in cathodic charging of group-VA metals: 1.12.6
- Hydrolysis of Mg₂Sn: 1.6.3.4.1
- Preparation of PdH: 1.12.7
- Protonation of Mg₂Si: 1.6.6.2
- Protonation of amines: 1.5.3.1.2
- Reactions with amides: 1.5.3.1.3
- Reaction with M(N₂)₂[P(CH₃)₂C₆H₅]₄ (M = Mo, W): 1.5.3.1.2
- Reaction with M(N₂)₂[PCH₃(C₆H₅)₂]₄ (M = Mo, W): 1.5.3.1.2

H₂O₈Os₂*C₈**H₂O₉Os₃S***C₉**H₂O₁₀Os₃***C₁₀**H₂O₁₁Os₃***C₁₂**H₂O₁₁Ru₃***C₁₁**H₂O₁₂Os₃***C₁₁**H₂O₁₃Ru₄***C₁₃**H₂O₁₈Os₆***C₁₈**H₂OsP₄***F₁₂**H₂P***Cs**H₂P***CsF₄**H₂P***F₃**H₂P₄***F₁₂Fe**H₂P₄Ru***F₁₂**H₂Pb₂**Pb₂H₂

- Formation: 1.6.3.5

H₂PrPrH₂

- Formation: 1.12.4.1

H₂Pt*Cl₆**H₂S**

- Cleavage of group-IVB-As

- bonds: 1.5.3.3.3

- Impurity in H₂: 1.8.2

- Reaction with [(CH₃)₂N]₃P: 1.5.3.2.3

- Reaction with dialkylaminodialkylphosphines: 1.5.3.2.3

H₂SO₄

- Reaction with CH₃CH=CH₂: 1.6.6.1

H₂STa₆Ta₆SH₂

- Preparation: 1.12.8.2.3

H₂ScScH₂

- Formation: 1.12.4.1

H₂Si*AsF₃**H₂Sm**SmH₂

- Formation: 1.12.4.1

H₂Sn(SnH₂)_n

- Formation: 1.6.3.4.2

H₂SrSrH₂

- Formation: 1.8.3.3

H₂TbTbH₂

- Formation: 1.12.4.1

H₂ThThH₂

- Formation: 1.12.4.2

H₂Th*C

- H₂Ti**
 TiH₂
 Formation: 1.12.5
H₂Ti*Fe
H₂Tm
 TmH₂
 Formation: 1.12.4.1
H₂Y
 YH₂
 Formation: 1.12.4.1
H₂Yb
 YbH₂
 Formation: 1.12.4.1
H₂Zn
 (ZnH₂)_n
 Formation: 1.9.4.2
H₂Zn
 (ZnH₂)_n
 Formation: 1.9.5.2
H₂Zn
 (ZnH₂)_n
 From reduction of ZnCl₂ by NaH or
 ZnBr₂ by LiH: 1.9.4.1
H₂Zr
 ZrH₂
 Formation: 1.12.5
H₃*Al
H₃*As
H₃AsCl₂*C
H₃*B
H₃BFe₄O₁₂*C₁₂
H₃BNNa*C
H₃BO₁₂Ru₄*C₁₂
H₃*Bi
H₃*Bi
H₃BiCl₂*C
H₃*BrGe
H₃Br₃Ge*C
H₃Cl*C
H₃Cl*C₂
H₃*ClGe
H₃ClO*C₂
H₃Cl₂P*C
H₃Cl₂Sb*C
H₃Cl₃Ge*C
H₃Cl₃Si*C
H₃Cl₃Sn*C
H₃Cl₉O₉Os₃Si₃*C₉
H₃CoO₁₂Ru₃*C₁₂
H₃Co₃O₁₀*C₁₂
H₃D*C
H₃D*C₂
H₃*DGe
- H₃D*Ge**
H₃F₃P₂*C
H₃F₅Hg*C₇
H₃I*Ge
H₃IZn*C
H₃I₂Zn*Al
H₃In
 InH₃
 Formation: 1.7.2
 (InH₃)_x
 Formation: 1.7.4.4
H₃K*Ge
H₃KO₂Sn*C
H₃KSi
K[SiH₃]K
 Formation: 1.6.4.2.3
 Reaction with hydrogen halides:
 1.6.3.2.3
 Formation: 1.6.4.2.3
H₃Li*C
H₃Li*Cu₂
H₃Li*Ge
H₃LiSi
 Li[SiH₃]
 Reaction with hydrogen halides:
 1.6.3.2.3
H₃LiZn
LiZnH₃
 Formation: 1.9.5.2
H₃Li₂*Cu
H₃N
NH₃
 Disproportionation in Ag₁₂-zeolite to
 N₃H₃, N₄H₄: 1.5.4.1.3
 Formation: 1.5.2.1.1, 1.5.2.1.2, 1.5.3.1.1,
 1.5.3.1.3, 1.5.4.1.2, 1.5.4.1.3, 1.5.5.1
 Impurity in H₂: 1.5.4.1.3
 Industrial synthesis from N₂ and H₂:
 1.5.6.1
 Liquid reaction medium: 1.9.5.2
 Oxidation in liq NH₃: 1.5.3.1.2
 Protonation in H₂O: 1.5.3.1.1
 Reaction with n-C₄H₉Li: 1.6.3.1.2
 Reaction with F₂PNH₂: 1.5.3.2.3
 Reaction with [(CH₃)₂N]₂PCl: 1.5.3.2.3
 Reaction with F₂PCl: 1.5.3.2.3
 Reaction with Zn(C₂H₅)₂: 1.6.3.1.2
 Reaction with trialkylgermanides:
 1.6.3.3.2
 Relative basicity: 1.5.3.1.3
 Self-association reaction: 1.5.3.1.2

H₃N *cont.*

Solvent for protonation of arsenides:

1.5.3.3.2

Solvent for stannide protonations:

1.6.3.4.2

H₃NO**H₂NOH**

Formation: 1.5.2.1.2, 1.5.3.1.1

Photolytic decomposition to NH₃:

1.5.4.1.3

Protonation in H₂O: 1.5.3.1.1**H₃NO₃S****HSO₃NH₂**

Formation: 1.5.3.1.1

H₃NO₄S**HONHSO₃H**Hydrolysis to NH₂OH: 1.5.3.1.1**H₃NO₆S₂****HN(SO₃H)₂**Hydrolysis to HSO₃NH₂: 1.5.3.1.1**H₃NO₁₁Os₃*C₁₃****H₃N₃****N₃H₃**

Formation: 1.5.4.1.3

H₃Na*Ge**H₃NaSi****Na[SiH₃]**

Reaction with hydrogen halides:

1.6.3.2.3

H₃NaZn**Na[ZnH₃]**

Formation: 1.9.4.2

From decomposition of Na[Zn₂H₃(C*H₃)₂]: 1.9.4.1**H₃O₂P****H₂P(O)OH**Action on CuSO₄: 1.9.5.2

Electrolysis: 1.5.3.2.1

H₃O₃*Ac**H₃O₃*B****H₃O₃*B₃****H₃O₃P****(HO)₂P(O)H**

Formation: 1.5.3.2.1, 1.5.3.2.2

Industrial formation: 1.5.6.2

Protonation in acid: 1.5.3.2.2

Thermal disproportionation: 1.5.3.2.3

H₃O₄P**H₃PO₄**Electrolyte in cathodic charging of
group-VA metals: 1.12.6

Reactions with amides: 1.5.3.1.3

H₃O₁₂Re₃*C₁₂**H₃P****PH₃**Exchange with acidic D₂O: 1.5.7.2.2

Formation: 1.5.3.2.1, 1.5.3.2.2, 1.5.4.2.1,

1.5.4.2.2, 1.5.5.2.1, 1.5.5.2.2

Formation from H₃PO₃: 1.5.3.2.3Formation from P₂H₄ pyrolysis:

1.5.4.2.4

Industrial formation from P₄ and aq

base: 1.5.6.2

Protonation in acid: 1.5.3.2.2

Reaction in silent electric discharge:

1.5.4.2.2

Reaction with GeH₄ in silent electric

discharge: 1.5.4.2.2

Reaction with PH₃: 1.6.4.2.1Reaction with SiH₄ in silent electric

discharge: 1.5.4.2.2, 1.6.4.2.3, 1.6.4.3.3

Reaction with carbon atoms: 1.6.2.1.1

H₃P*F₂**H₃S₆*B₃****H₃Sb****SbH₃**

Formation: 1.5.2.4, 1.5.3.4, 1.5.5.4

Formation by Na[BH₄] reduction of

Sb*

(III) salts: 1.5.6.4

Industrial synthesis by electrochemical

reduction: 1.5.6.4

H₃Si*Cl**H₃Si*D****H₃U****UH₃**

Formation: 1.12.4.2

H₃Zn₂*Br**H₄*AgAl****H₄*AgB****H₄*AgGa****H₄*AlCs****H₄*AlCu****H₄AlLiO*C****H₄AlLiO₄*C₂****H₄AlLiO₈*C₄****H₄AsCl*C****H₄AsF₃P₂*C****H₄AsO₄*C₅****H₄*As₂****H₄BLiO₄*C₂****H₄BNaO₆*C₃****H₄*B₁₀D₄****H₄*B₁₀D₁₀**

- $\text{H}_4\text{BrNO}_2 \cdot \text{C}_4$
 $\text{H}_4\text{BrO}_5\text{Re} \cdot \text{C}_6$
 $\text{H}_4 \cdot \text{C}$
 $\text{H}_4 \cdot \text{C}_2$
 $\text{H}_4 \cdot \text{C}_3$
 $\text{H}_4 \cdot \text{C}_4$
 $\text{H}_4\text{ClNO}_3 \cdot \text{C}_7$
 $\text{H}_4\text{Cl}_3\text{Si} \cdot \text{C}$
 $\text{H}_4\text{Cl}_4\text{N}_3\text{P}_3 \cdot \text{C}$
 $\text{H}_4\text{Cl}_4\text{Si} \cdot \text{C}_2$
 $\text{H}_4\text{F}_2\text{Ge} \cdot \text{C}$
 $\text{H}_4\text{F}_3\text{NO}_9\text{Os}_3 \cdot \text{C}_{11}$
 $\text{H}_4\text{F}_3\text{NO}_{10}\text{Os}_3 \cdot \text{C}_{12}$
 $\text{H}_4\text{F}_3\text{P} \cdot \text{C}$
 $\text{H}_4\text{F}_3\text{P}_3 \cdot \text{C}$
 $\text{H}_4\text{F}_7\text{N}_2\text{P} \cdot \text{C}_6$
 $\text{H}_4\text{FeO}_{12}\text{Os}_3 \cdot \text{C}_{12}$
 $\text{H}_4\text{FeO}_{12}\text{Ru}_3 \cdot \text{C}_{12}$
 $\text{H}_4\text{Fe}_3\text{O}_{11} \cdot \text{C}_{12}$
 $\text{H}_4 \cdot \text{Ge}$
 $\text{H}_4\text{GeO}_2 \cdot \text{C}$
 H_4IN
 $[\text{NH}_4]\text{I}$
 Reaction with CaSn : 1.6.3.4.2
 H_4IP
 $[\text{PH}_4]\text{I}$
 Formation: 1.5.3.2.3
 H_4InLi
 $\text{Li}[\text{InH}_4]$
 Formation: 1.7.4.4
 $\text{H}_4\text{InLi} \cdot \text{AlCl}_3$
 $\text{H}_4\text{InLi} \cdot \text{BCl}_3$
 $\text{H}_4\text{K} \cdot \text{Al}$
 $\text{H}_4\text{K} \cdot \text{B}$
 $\text{H}_4\text{KSi} \cdot \text{As}$
 $\text{H}_4\text{K}_2\text{Zn}$
 $\text{K}_2[\text{ZnH}_4]$
 Formation: 1.9.4.2
 $\text{H}_4\text{Li} \cdot \text{Al}$
 $\text{H}_4\text{Li} \cdot \text{Al}$
 $\text{H}_4\text{Li} \cdot \text{Al}$
 $\text{H}_4\text{Li} \cdot \text{B}$
 $\text{H}_4\text{Li} \cdot \text{Ga}$
 H_4LiPSi
 H_3SiPHLi
 Redistribution to LiPH_2 and $(\text{SiH}_3)_2\text{P}^*$
 Li: 1.5.4.2.4
 H_4LiP_5
 LiH_4P_5
 Disproportionation to Li_2HP_7 , P_2H_4
 and PH_3 : 1.5.4.2.4
 H_4LiTi
 LiTiH_4
 Formation: 1.7.4.5
 $\text{H}_4\text{Li}_2\text{Zn}$
 Li_2ZnH_4
 Formation: 1.9.5.2
 $\text{H}_4\text{Li}_3 \cdot \text{Cu}$
 H_4MgN_2
 $\text{Mg}(\text{NH}_2)_2$
 Hydrolysis to NH_3 : 1.5.3.1.1
 H_4MgZn
 MgZnH_4
 Formation: 1.9.5.2
 $\text{H}_4\text{N} \cdot \text{Br}$
 $\text{H}_4\text{N} \cdot \text{Cl}$
 H_4N_2
 N_2H_4
 Disproportionation: 1.5.4.1.3
 Formation: 1.5.2.1.1, 1.5.2.1.2, 1.5.3.1.1,
 1.5.3.1.2, 1.5.3.1.3, 1.5.4.1.3
 Protonation in H_2O : 1.5.3.1.1
 $\text{H}_4\text{N}_2 \cdot \text{Ba}$
 $\text{H}_4\text{N}_2 \cdot \text{Ca}$
 $\text{H}_4\text{N}_2 \cdot \text{Cd}$
 $\text{H}_4\text{N}_2\text{O} \cdot \text{C}$
 $\text{H}_4\text{N}_2\text{O}_2 \cdot \text{C}$
 $\text{H}_4\text{N}_2\text{O}_2\text{S}$
 $\text{O}_2\text{S}(\text{NH}_2)_2$
 Formation: 1.5.4.1.3
 $\text{H}_4\text{N}_2\text{O}_6\text{S} \cdot \text{C}_2$
 $\text{H}_4\text{N}_4\text{Sr}$
 $\text{Sr}(\text{NH}_2)_2$
 Reaction with H_2O : 1.5.3.1.3
 $\text{H}_4\text{N}_4\text{Zn}$
 $\text{Zn}(\text{NH}_2)_2$
 Hydrolysis to NH_3 : 1.5.3.1.1
 Reaction with H_2O : 1.5.3.1.3
 H_4N_4
 N_4H_4
 Formation: 1.5.3.1.3, 1.5.4.1.3
 $\text{H}_4\text{Na} \cdot \text{Al}$
 $\text{H}_4\text{Na} \cdot \text{AlB}$
 $\text{H}_4\text{Na} \cdot \text{B}$
 $\text{H}_4\text{O} \cdot \text{C}$
 $\text{H}_4\text{O} \cdot \text{C}_2$
 $\text{H}_4\text{O} \cdot \text{C}_4$
 $\text{H}_4\text{OSi} \cdot \text{C}$
 $\text{H}_4\text{O}_2 \cdot \text{C}_2$
 $\text{H}_4\text{O}_2\text{P} \cdot \text{C}$
 $\text{H}_4\text{O}_4\text{Os} \cdot \text{C}_5$
 $\text{H}_4\text{O}_4\text{P}_2 \cdot \text{Ba}$
 $\text{H}_4\text{O}_9\text{Os}_3 \cdot \text{C}_{11}$

- $\text{H}_4\text{O}_{11}\text{Os}_3^*\text{C}_{11}$
 $\text{H}_4\text{O}_{11}\text{Os}_3^*\text{C}_{12}$
 $\text{H}_4\text{O}_{11}\text{Ru}_3^*\text{C}_{12}$
 $\text{H}_4\text{O}_{12}\text{Os}_4^*\text{C}_{12}$
 $\text{H}_4\text{O}_{12}\text{Re}_4^*\text{C}_{12}$
 $\text{H}_4\text{O}_{12}\text{Ru}_4^*\text{C}_{12}$
 $\text{H}_4\text{O}_{16}\text{Re}_4^*\text{C}_{12}$
 $\text{H}_4\text{P}^*\text{As}$
 $\text{H}_4\text{P}^*\text{Br}$
 $\text{H}_4\text{P}^*\text{Cl}$
 H_4P_2
 P_2H_4
 Formation: 1.5.2.2, 1.5.3.2.1, 1.5.3.2.2,
 1.5.4.2.4, 1.6.4.2.3, 1.6.4.3.3
 Formation from PH_3 in silent electric
 discharge: 1.5.4.2.2
 Formation in PH_3 pyrolysis: 1.5.4.2.2
 Pyrolysis in hot-cold reactor: 1.5.4.2.4
 Reaction with $n\text{-C}_4\text{H}_9\text{Li}$: 1.5.4.2.4
 H_4Pb
 PbH_4
 Formation: 1.6.3.5
 H_4Si
 SiH_4
 Exchange with DCl in presence of
 AlCl_3 : 1.6.7.2.2
 Exchange with D_2 : 1.6.7.2.2
 Formation: 1.6.3.2.1, 1.6.3.2.2, 1.6.3.2.3,
 1.6.4.2.1, 1.6.4.2.2, 1.6.4.2.3, 1.6.5.2.1,
 1.6.5.2.2, 1.6.5.2.3
 Formation in $\text{H}_2\text{-SiO}_2$ reaction: 1.6.2.2
 Industrial formation: 1.6.6.2
 Pyrolysis in presence of GeH_4 : 1.6.4.2.3
 Reaction with AsH_3 in silent electric
 discharge: 1.5.4.3, 1.6.4.2.3
 Reaction with GeH_4 in silent electric
 discharge: 1.6.4.2.3, 1.6.4.3.3
 Reaction with PH_3 in silent electric dis-
 charge: 1.5.4.2.2, 1.6.4.2.3
 Reaction with Si atoms: 1.6.2.2
 Reaction with $[\text{CH}_3]^+$: 1.6.4.2.3
 Reaction with hydrogen atoms: 1.6.2.2
 Thermolysis in presence of GeH_4 :
 1.6.4.3.3
 H_4Sn
 SnH_4
 Formation: 1.6.2.4, 1.6.3.4.1, 1.6.3.4.2,
 1.6.4.4.2, 1.6.5.4.1, 1.6.5.4.2
 $\text{H}_4\text{Th}_3^*\text{C}$
 $\text{H}_4\text{Tl}^*\text{B}$
 $\text{H}_5\text{As}^*\text{C}$
 H_5^*AsGe
- $\text{H}_5^*\text{B}_2\text{Br}$
 $\text{H}_5^*\text{B}_2\text{Cl}$
 $\text{H}_5\text{BiBr}_2^*\text{C}_6$
 $\text{H}_5\text{Bi}^*\text{C}$
 $\text{H}_5\text{Br}^*\text{C}_2$
 $\text{H}_5\text{BrMg}^*\text{C}_2$
 $\text{H}_5\text{Cl}^*\text{C}_8$
 $\text{H}_5\text{ClMg}^*\text{C}_2$
 $\text{H}_5\text{ClMoO}_3^*\text{C}_8$
 $\text{H}_5\text{ClN}_2\text{O}_2\text{W}^*\text{C}_5$
 $\text{H}_5\text{Cl}_2\text{OP}^*\text{C}_6$
 $\text{H}_5\text{Cl}_2\text{P}^*\text{C}_2$
 $\text{H}_5\text{Cl}_2\text{P}^*\text{C}_6$
 $\text{H}_5\text{Cl}_2\text{Sb}^*\text{C}_2$
 $\text{H}_5\text{Cl}_3\text{Ge}^*\text{C}_2$
 $\text{H}_5\text{Cl}_3\text{Ge}^*\text{C}_6$
 $\text{H}_5\text{Cl}_3\text{Si}^*\text{C}_2$
 $\text{H}_5\text{Cl}_3\text{Si}^*\text{C}_3$
 $\text{H}_5\text{Cl}_3\text{Si}^*\text{C}_6$
 $\text{H}_5\text{Cl}_3\text{Sn}^*\text{C}_2$
 $\text{H}_5\text{Cl}_3\text{Sn}^*\text{C}_6$
 $\text{H}_5\text{Co}_3\text{O}_9^*\text{C}_{12}$
 $\text{H}_5\text{Co}_3\text{O}_9^*\text{C}_{13}$
 $\text{H}_5\text{Co}_3\text{O}_{10}^*\text{C}_{13}$
 $\text{H}_5\text{Co}_3\text{O}_{10}^*\text{C}_{17}$
 $\text{H}_5\text{D}^*\text{C}_2$
 $\text{H}_5\text{D}^*\text{C}_6$
 $\text{H}_5\text{DO}^*\text{C}_2$
 $\text{H}_5\text{D}_2\text{N}^*\text{C}_3$
 $\text{H}_5\text{D}_2\text{N}^*\text{C}_6$
 $\text{H}_5\text{D}_2\text{P}^*\text{C}_6$
 $\text{H}_5\text{D}_3^*\text{C}_7$
 $\text{H}_5\text{D}_3\text{O}^*\text{C}_3$
 $\text{H}_5\text{D}_3\text{O}^*\text{C}_7$
 $\text{H}_5\text{D}_4\text{N}^*\text{C}_7$
 $\text{H}_5\text{FGe}^*\text{C}$
 $\text{H}_5\text{F}_2\text{N}^*\text{C}_2$
 $\text{H}_5\text{F}_2\text{P}^*\text{C}_3$
 $\text{H}_5\text{F}_2\text{P}^*\text{C}_6$
 $\text{H}_5\text{F}_3\text{O}_5\text{W}^*\text{C}_{10}$
 $\text{H}_5\text{F}_6\text{MoO}_3\text{P}^*\text{C}_8$
 $\text{H}_5\text{F}_6\text{NO}_3\text{PRe}^*\text{C}_7$
 $\text{H}_5\text{F}_6\text{N}_2\text{P}^*\text{C}_6$
 $\text{H}_5\text{FeNaO}_2^*\text{C}_7$
 $\text{H}_5\text{I}^*\text{C}_2$
 $\text{H}_5\text{I}^*\text{C}_6$
 $\text{H}_5\text{I}^*\text{Ge}_2$
 $\text{H}_5\text{I}_2\text{Sb}^*\text{C}_6$
 H_5KZn_2
 KZn_2H_5
 Formation: 1.9.5.2
 $\text{H}_5\text{Li}^*\text{C}_2$

- $\text{H}_5\text{Li}^*\text{C}_5$
 $\text{H}_5\text{Li}_2^*\text{Cu}_3$
 $\text{H}_5\text{Li}_3\text{Zn}$
 Li_3ZnH_5
 Formation: 1.9.5.2
 $\text{H}_5\text{Li}_4^*\text{Cu}$
 $\text{H}_5\text{MoNaO}_3^*\text{C}_8$
 $\text{H}_5\text{N}^*\text{C}$
 $\text{H}_5\text{N}^*\text{C}_3$
 $\text{H}_5\text{N}^*\text{C}_5$
 $\text{H}_5\text{N}^*\text{C}_7$
 $\text{H}_5\text{N}^*\text{F}_2$
 $\text{H}_5\text{NO}^*\text{C}_6$
 $\text{H}_5\text{NO}^*\text{C}_7$
 $\text{H}_5\text{NO}_2^*\text{C}_2$
 $\text{H}_5\text{NO}_3^*\text{C}_3$
 $\text{H}_5\text{NO}_2^*\text{C}_4$
 $\text{H}_5\text{NO}_2^*\text{C}_6$
 $\text{H}_5\text{NO}_3^*\text{C}_7$
 $\text{H}_5\text{NS}^*\text{C}_3$
 $\text{H}_5\text{N}_2\text{P}^*\text{F}_2$
 H_5N_3
 N_3H_5
 Formation: 1.5.4.1.3
 $\text{H}_5\text{Na}_2\text{NbO}_3^*\text{C}_8$
 $\text{H}_5\text{Na}_2\text{P}^*\text{C}_6$
 $\text{H}_5\text{NbO}_4^*\text{C}_9$
 $\text{H}_5\text{Nb}_{21}\text{S}_8$
 $\text{Nb}_{21}\text{S}_8\text{H}_5$
 Preparation: 1.12.8.2.3
 $\text{H}_5\text{OTi}^*\text{C}_2$
 $\text{H}_5\text{O}_2\text{P}^*\text{C}$
 $\text{H}_5\text{O}_2\text{Rh}^*\text{C}_7$
 $\text{H}_5\text{O}_3\text{Re}^*\text{C}_8$
 $\text{H}_5\text{O}_4\text{V}^*\text{C}_9$
 $\text{H}_5\text{O}_3\text{Rh}^*\text{C}_6$
 $\text{H}_5\text{P}^*\text{C}$
 $\text{H}_5\text{P}^*\text{Ge}$
 H_5PSi
 H_3SiPH_2
 Disproportionation catalyzed by BF_3 :
 1.5.4.2.4
 Formation from PH_3 and SiH_4 in silent electric discharge: 1.5.4.2.2
 Hydrolysis: 1.5.3.2.3
 Pyrolysis in the presence of $(\text{CH}_3)_2\text{SiD}_2$:
 1.5.4.2.4
 Thermolysis to PH_3 and SiH_4 : 1.5.4.2.4
 H_5P_3
 P_3H_5
 Formation from P_2H_4 pyrolysis:
 1.5.4.2.4
- H_5P_5
 P_5H_5
 Formation: 1.5.3.2.3
 $\text{H}_5\text{Sb}^*\text{C}$
 $\text{H}_5\text{Si}^*\text{As}$
 $\text{H}_5\text{Si}^*\text{C}_3$
 $\text{H}_6\text{AgBO}_2^*\text{C}_2$
 $\text{H}_6\text{AsCrF}_6\text{PO}_5^*\text{C}_9$
 $\text{H}_6\text{AsF}_3\text{Si}^*\text{C}_2$
 $\text{H}_6\text{AsF}_6\text{MoO}_5\text{PO}_5^*\text{C}_9$
 $\text{H}_6\text{As}_2\text{CrF}_6\text{O}_5^*\text{C}_9$
 $\text{H}_6\text{As}_2\text{F}_6\text{MoO}_5^*\text{C}_9$
 $\text{H}_6\text{BClO}_2^*\text{C}_2$
 H_6^*B_2
 $\text{H}_6\text{B}_3\text{Fe}_2\text{O}_6^*\text{C}_6$
 $\text{H}_6^*\text{B}_{10}\text{D}_8$
 $\text{H}_6\text{Be}^*\text{C}_2$
 $\text{H}_6\text{BiCl}^*\text{C}_2$
 $\text{H}_6\text{BrSb}^*\text{C}_2$
 $\text{H}_6\text{Br}_2\text{D}_2^*\text{C}_8$
 H_6^*C_2
 H_6^*C_3
 H_6^*C_4
 H_6^*C_5
 H_6^*C_6
 H_6^*C_8
 $\text{H}_6\text{Cd}^*\text{C}_2$
 $\text{H}_6\text{ClD}^*\text{C}_3$
 $\text{H}_6\text{ClO}_2\text{P}^*\text{C}_2$
 $\text{H}_6\text{ClP}^*\text{C}_2$
 $\text{H}_6\text{ClSb}^*\text{C}_2$
 $\text{H}_6\text{ClZr}^*\text{C}_5$
 $\text{H}_6\text{Cl}_2\text{Ge}^*\text{C}_2$
 $\text{H}_6\text{Cl}_2\text{OSi}^*\text{C}_2$
 $\text{H}_6\text{Cl}_2\text{Pb}^*\text{C}_2$
 $\text{H}_6\text{Cl}_2\text{Si}^*\text{C}_2$
 $\text{H}_6\text{Cl}_2\text{Sn}^*\text{C}_2$
 $\text{H}_6\text{Cl}_4\text{N}_3\text{P}_3^*\text{C}_2$
 $\text{H}_6\text{Co}_3\text{F}_6\text{O}_9\text{P}^*\text{C}_{13}$
 $\text{H}_6\text{CrF}_6\text{O}_5\text{P}_2^*\text{C}_9$
 $\text{H}_6\text{CrO}_3^*\text{C}_8$
 $\text{H}_6\text{CrO}_3^*\text{C}_9$
 $\text{H}_6\text{DN}^*\text{C}_2$
 $\text{H}_6\text{DP}^*\text{C}_2$
 $\text{H}_6\text{D}_2\text{O}^*\text{C}_3$
 $\text{H}_6\text{D}_2\text{O}^*\text{C}_7$
 $\text{H}_6\text{D}_2\text{Si}^*\text{C}_2$
 $\text{H}_6\text{FOP}^*\text{C}_6$
 $\text{H}_6\text{F}_2\text{Ge}^*\text{C}_2$
 $\text{H}_6\text{F}_2\text{Ge}^*\text{C}_6$
 $\text{H}_6\text{F}_2\text{NP}^*\text{C}_2$
 $\text{H}_6\text{F}_3\text{NO}_8\text{Os}_3^*\text{C}_{10}$

$H_6F_3P^*C_2$
 $H_6F_3P^*C_3$
 $H_6F_4FeO_2^*C_9$
 $H_6F_6MoO_5P_2^*C_9$

$H_6F_6P_2^*C_4$
 $H_6FeO_2^*C_7$
 $H_6FeO_3^*C_7$
 $H_6FeO_4^*C_8$
 $H_6Fe_3O_{10}^*C_{11}$

H_6Ge^*C
 $H_6GeS^*C_2$
 $H_6^*Ge_2$
 H_6K^*BGe

H_6LaNi_8

$LaNi_5H_6$

Formation: 1.12.8.1.1

Pseudobinary metallic hydride: 1.12.1

H_6LiPSi_2

$(SiH_3)_2PLi$

Formation from SiH_3PHLi redistribution: 1.5.4.2.4

$H_6LiSb^*C_2$

$H_6Mg^*C_2$

$H_6MoO_3^*C_8$

H_6N^*B

$H_6NNa^*C_2$

$H_6NO_2Re^*C_6$

$H_6NO_3Re^*C_7$

$H_6NO_4Re^*C_7$

$H_6NP^*C_3$

$H_6N_2^*C_3$

$H_6N_2O_2^*C$

$H_6N_2O_2W^*C_5$

$H_6N_2O_{10}Os_3^*C_{14}$

$H_6N_3^*B_3$

H_6N_3OP

$(NH_2)_3PO$

Hydrolysis in aq base: 1.5.3.1.1

Redistribution: 1.5.4.1.3

H_6N_4

N_4H_6

Disproportionation to NH_3 : 1.5.4.1.3

$H_6N_6^*C_3$

$H_6NaNbO_3^*C_8$

$H_6O^*C_2$

$H_6O^*C_3$

$H_6O^*C_7$

$H_6O^*Ge_2$

H_6OSi_2

$(SiH_3)_2O$

Reduction with B_2H_6 : 1.6.4.2.2

$H_6O_2^*C_2$

$H_6O_2^*C_6$

$H_6O_2^*C_7$

$H_6O_2Ru^*C_7$

$H_6O_3Si_6$

$(Si_6H_6O_3)_n$

Formation: 1.6.3.2.1

$H_6O_3W^*C_8$

$H_6O_{10}Os_3^*C_{11}$

$H_6O_{10}Os_3S^*C_{12}$

$H_6O_{10}Ru_3^*C_{11}$

$H_6O_{10}Ru_3S^*C_{12}$

$H_6P_2^*C$

H_6Si^*C

$H_6Si^*C_2$

H_6Si^*Ge

H_6Si_2

Si_2H_6

Formation: 1.6.2.2, 1.6.3.2.1, 1.6.4.2.1,

1.6.4.2.3, 1.6.5.2.1, 1.6.7.1.2

Formation from SiH_4 or SiH_4-PH_3 mixtures in silent electric discharge:

1.5.4.2.2

Formation in $H-SiH_4$ reaction: 1.6.2.2

Hg-photosensitized reaction: 1.6.4.2.3

Pyrolysis in presence of Ge_2H_6 : 1.6.4.2.3

Reaction with Si atoms in a matrix:

1.6.2.2

Reaction with CH_3SiH_3 : 1.6.4.2.3

Reaction with KH : 1.6.4.2.3

Thermolysis: 1.6.4.2.3

Thermolysis in presence of Ge_2H_6 :

1.6.4.3.3

H_6Sn^*C

$H_6Sn^*C_2$

H_6Sn^*Ge

H_6Sn_2

Sn_2H_6

Formation: 1.6.5.4.1, 1.6.5.4.2

$H_6Zn^*C_2$

$H_7As^*C_2$

$H_7As^*C_6$

$H_7AsCrO_5^*C_7$

$H_7AsF_6^*C_6$

H_7AsGe^*C

$H_7AsMoO_5^*C_7$

$H_7AsO^*C_2$

$H_7AsO_2^*C_2$

$H_7AsO_2^*C_6$

H_7AsSi^*C

$H_7BO_2^*C_2$

H_7BZn^*C

$H_7B_5^*C_2$

$H_7Bi^*C_2$
 $H_7Br^*C_3$
 $H_7Br^*C_7$
 $H_7Cl^*C_7$
 $H_7Cl^*C_8$
 $H_7ClFeO_3^*C_7$
 $H_7ClFeO_4^*C_8$
 $H_7ClGe^*C_2$
 $H_7ClMg^*C_3$
 $H_7ClO_2Si^*C_2$
 $H_7ClSi^*C_2$
 $H_7ClSn^*C_2$
 $H_7Cl_2N^*C_7$
 $H_7Cl_2P^*C_3$
 $H_7Cl_2P^*C_7$
 $H_7CoN_2O_2^*C_7$
 $H_7Co_3O_9^*C_{13}$
 $H_7Co_3O_9^*C_{17}$
 $H_7CrPO_5^*C_7$
 $H_7D^*C_3$
 $H_7D^*C_7$
 $H_7D^*C_{10}$
 $H_7D_2PSi^*C_2$
 $H_7FGe^*C_2$
 $H_7F_6N_2P^*C_7$
 $H_7F_8OP^*C_9$
 $H_7Fe_4NO_{13}^*C_{18}$
 H_7GeP^*C
 $H_7KZn^*C_2$
 $H_7Li^*B_2$
 $H_7Li^*C_3$
 $H_7MnO_3^*C_9$
 $H_7MoPO_5^*C_7$
 $H_7N^*C_2$
 $H_7N^*C_2$
 $H_7N^*C_2$
 $H_7N^*C_2$
 $H_7N^*C_2$
 $H_7N^*C_6$
 $H_7NO^*C_7$
 $H_7NO_9Os_3^*C_{15}$
 $H_7NO_{10}Os_3^*C_{16}$
 $H_7Na^*B_2$
 $H_7Na^*C_{10}$
 $H_7Na^*C_{10}$
 $H_7OP^*C_2$
 $H_7O_2^*C_4$
 $H_7O_2P^*C_2$
 $H_7O_2P^*C_6$
 $H_7O_2Re^*C_7$
 $H_7O_3P^*C_2$
 $H_7O_3P^*C_6$

$H_7P^*C_2$
 $H_7P^*C_6$
 $H_7P^*Ge_2$
 $H_7PS^*C_2$
 $H_7PSi^*C_2$
 H_7PSi_2
 $(SiH_3)_2PH$
 Formation: 1.6.4.2.3
 Reaction with D_2O : 1.5.7.1.2
 $Si_2H_5PH_2$
 Disproportionation catalyzed by BF_3 :
 1.5.4.2.4
 Formation: 1.6.4.2.3
 Formation from SiH_4 - PH_3 mixtures in
 silent electric discharge: 1.5.4.2.2
 Thermolysis: 1.5.4.2.4
 $H_7Sb^*C_2$
 $H_7Sb^*C_6$
 $H_7Si^*C_2$
 $H_7W^*C_5$
 $H_8AlNaO^*C_2$
 $H_8BCl_2N^*C_7$
 $H_8BP^*C_2$
 $H_8^*B_2Be$
 $H_8B_2^*C$
 $H_8^*B_2Ca$
 $H_8^*B_2Cd$
 $H_8^*B_3Cu$
 $H_8^*B_4D_2$
 $H_8^*B_5Cl$
 $H_8^*B_4D$
 $H_8^*B_6D_4$
 $H_8^*B_{10}D_6$
 $H_8B_{10}O_2^*C_2$
 $H_8^*C_3$
 $H_8^*C_4$
 $H_8^*C_7$
 $H_8^*C_8$
 $H_8^*C_{10}$
 $H_8ClP^*C_2$
 $H_8ClW^*C_5$
 $H_8Cl_2NO_4PS^*C_{12}$
 $H_8Cl_4N_3P_3^*C_3$
 $H_8D_2O^*C_8$
 $H_8F_5OP^*C_8$
 $H_8FeO_3^*C_8$
 $H_8Ge^*C_2$
 $H_8Ge^*C_5$
 $H_8Ge^*C_6$
 $H_8GeP_2^*C$
 $H_8^*Ge_3$
 $H_8HgO_2^*C_8$

$H_8Li*AlAs_4$
 $H_8MoO_3*C_{11}$
 $H_8NO_2Re*C_7$
 $H_8NO_3Re*C_7$
 H_8NP*C_6
 $H_8N_2*C_2$
 $H_8NiO_9Ru_3*C_{14}$
 H_8O*C_3
 H_8O*C_4
 H_8O*C_7
 H_8O*C_8
 H_8OSi*C_2
 $H_8O_2*C_4$
 $H_8O_2Si*C_2$
 $H_8O_4S*C_3$
 $H_8P_2*C_2$
 H_8Pb*C_2
 H_8Si*C_2
 H_8Si*C_3
 H_8Si*C_6
 H_8Si*Ge_2
 H_8Si_2*C
 H_8Si_2*Ge
 H_8Si_3

Si_3H_8

Formation: 1.6.2.2, 1.6.3.2.1, 1.6.4.2.3,
1.6.5.2.1

Formation from SiH_4 in silent electric
discharge: 1.5.4.2.2

Formation in $H-SiH_4$ reaction: 1.6.2.2

Pyrolysis in presence of Ge_2H_6 :

1.6.4.2.3, 1.6.4.3.3

H_8Sn*C_2
 H_8Sn*C_6
 H_8Ti*B_2Cl
 H_8Zn*B_2
 H_9Al*C_3
 $H_9AlClLi*C_8$
 H_9As*C_7
 H_9*AsGe_3
 H_9AsO*C_7
 $H_9AsO_2*C_7$
 $H_9AsO_4*C_7$
 H_9B*C_6
 $H_9BF_7N_2O_2Re*C_{14}$
 $H_9BO_3*C_3$
 H_9*B_2Ga
 H_9*B_4D
 H_9*B_5
 $H_9B_5FeO_3*C_3$
 $H_9BrGe*C_3$
 $H_9BrMg*C_4$

$H_9BrSn*C_3$
 $H_9ClGe*C_3$
 $H_9ClPb*C_3$
 $H_9ClSi*C_3$
 $H_9ClSn*C_3$
 $H_9Cl_2P*C_4$
 $H_9Cl_2Sb*C_4$
 $H_9Cl_3Sn*C_4$
 $H_9Cl_5NSb*C_6$
 H_9D*C_4
 $H_9D_2NSi*C_3$
 $H_9F_2OP*C_7$
 $H_9F_5NP*C_2$
 $H_9F_6NSn*C_6$
 $H_9FeNO_2*C_{10}$
 H_9Ga*C_3
 $H_9GeN_3*C_3$
 H_9GeP*C_2
 H_9In*C_3
 H_9K*B_4
 H_9K*B_6
 $H_9K*B_9D_5$
 H_9Li*C_4
 $H_9MoNO_4P*C_6$
 H_9N*C_7
 H_9N*C_8
 H_9NO*C_8
 $H_9NO_2*C_4$
 $H_9NO_{10}Ru_3*C_{15}$
 $H_9NO_{11}Ru_3*C_{16}$
 $H_9NPS_3*C_2$
 H_9NSi_3

$(H_3Si)_3N$

Disproportionation in presence of B_5H_9 :
1.6.4.2.3

Disproportionation in presence of NH_3 :
1.6.3.2.2, 1.6.4.2.3

$H_9N_3*C_{12}$
 $H_9N_3Si*C_3$
 $H_9NaSn*C_3$
 $H_9NaZn_2*C_2$
 H_9Na_2Re

$Na_2[ReH_9]$

Formation from Na and EtOH: 1.10.8.1

H_9OP*C_7
 $H_9O_2P*C_3$
 $H_9O_2P*C_7$
 $H_9O_3P*C_3$
 $H_9O_3P*C_6$
 $H_9O_3Re*C_9$
 H_9P*C_7
 H_9P*C_8

$H_9P^*Ge_3$	$H_{10}Cl_2Si^*C_{12}$
H_9PSi_3	$H_{10}Cl_2Sn^*C_4$
$(H_3Si)_3P$	$H_{10}Cl_2Sn^*C_{12}$
Cleavage by $trans-Pt(H)[P(C_2H_5)_3]_2$:	$H_{10}Cl_2Ti^*C_4$
1.5.4.2.2	$H_{10}Cl_2Zr^*C_{10}$
Formation in $Si_2H_5PH_2$ thermolysis:	$H_{10}Cl_3P^*C_{12}$
1.5.4.2.4	$H_{10}Cr_2O_6^*C_{16}$
$H_9Sb^*Ge_3$	$H_{10}DP^*C_{12}$
H_9SbSi_3	$H_{10}D_2Si^*C_{12}$
$(H_3Si)_3Sb$	$H_{10}F_2GeSi^*C_3$
Cleavage by HCl : 1.5.3.4	$H_{10}F_2OP^*C_5$
$H_9Si_3^*As$	$H_{10}F_2O_2Si^*C_4$
$H_{10}AlD^*C_4$	$H_{10}F_2Si^*C_4$
$H_{10}AlLiZn^*C_2$	$H_{10}F_3N_2O_2Re^*C_{14}$
$H_{10}AsCl^*C_{13}$	$H_{10}F_3P^*C_4$
$H_{10}AsK_2N^*C_4$	$H_{10}Fe^*C_{10}$
$H_{10}BF_4N^*C_3$	$H_{10}FeNO_2^*C_{10}$
$H_{10}BGa^*C_2$	$H_{10}FeO_2^*C_{10}$
$H_{10}BK^*C_3$	$H_{10}Fe_2O_4^*C_{14}$
$H_{10}BLiO_3^*C_3$	$H_{10}Ge^*C_3$
$H_{10}BLiO_5^*C_4$	$H_{10}Ge^*C_4$
$H_{10}BNaO_3^*C_3$	$H_{10}GeP_2^*C_2$
$H_{10}BO_3^*C_3$	$H_{10}Ge_2^*C_2$
$H_{10}BP^*C_2$	$H_{10}^*Ge_4$
$H_{10}BZr^*C_5$	$H_{10}LiP^*C_4$
$H_{10}^*B_4$	$H_{10}LiP^*C_{12}$
$H_{10}^*B_6$	$H_{10}LiSb^*C_4$
$H_{10}^*B_{10}Cu_2$	$H_{10}LiSb^*C_{12}$
$H_{10}^*B_{10}D_4$	$H_{10}Mg^*C_4$
$H_{10}BiCl^*C_{12}$	$H_{10}Mg^*C_{14}$
$H_{10}BrSb^*C_4$	$H_{10}N^*C_5$
$H_{10}Br_2Ge^*C_{12}$	$H_{10}NOP^*C_8$
$H_{10}^*C_4$	$H_{10}NO_3P^*C_8$
$H_{10}^*C_5$	$H_{10}N_2^*C_{13}$
$H_{10}^*C_6$	$H_{10}N_2O_2Ti^*C_4$
$H_{10}^*C_8$	$H_{10}N_2O_4^*C_6$
$H_{10}^*C_9$	$H_{10}N_4Si^*C_4$
$H_{10}ClD_2Fe_2O_4P^*C_{14}$	$H_{10}NaP^*C_{12}$
$H_{10}ClMgN_2Ti^*C_{10}$	$H_{10}Ni_2O_2^*C_{12}$
$H_{10}ClOP^*C_5$	$H_{10}O^*C_4$
$H_{10}ClOP^*C_{10}$	$H_{10}O^*C_5$
$H_{10}ClOP^*C_{12}$	$H_{10}O^*C_8$
$H_{10}ClP^*C_{12}$	$H_{10}OSi^*C_3$
$H_{10}ClP^*C_{13}$	$H_{10}OW^*C_{11}$
$H_{10}ClSb^*C_{12}$	$H_{10}O_2Ti^*C_4$
$H_{10}Cl_2Fe_2GeO_4^*C_{14}$	$H_{10}O_2Ti^*C_{12}$
$H_{10}Cl_2Ge^*C_4$	$H_{10}O_2Zr^*C_{12}$
$H_{10}Cl_2Ge^*C_{12}$	$H_{10}O_3Rh_2^*C_{13}$
$H_{10}Cl_2Nb^*C_{10}$	$H_{10}O_6W_2^*C_{16}$
$H_{10}Cl_2O_2Si^*C_4$	$H_{10}O_9Ru_3^*C_{15}$
$H_{10}Cl_2Pb^*C_4$	$H_{10}P_2^*C_3$
$H_{10}Cl_2Si^*C_4$	$H_{10}P_2^*C_7$

- $H_{10}Pb^*C_3$
 $H_{10}Pb^*C_6$
 $H_{10}Si^*C_3$
 $H_{10}Si^*Ge_3$
 $H_{10}Si_2^*C_2$
 $H_{10}Si_2^*C_3$
 $H_{10}Si_2^*Ge_2$
 $H_{10}Si_3^*Ge$
 $H_{10}Si_4$
 $(H_3Si)_2SiHSiH_3$
 Formation: 1.6.3.2.1, 1.6.4.2.3, 1.6.5.2.1
 Formation in H-SiH₄ reaction: 1.6.2.2
 Reaction with Ge₃H₈: 1.6.4.3.3
 $H_{10}Si_5$
 $(SiH_2)_5$
 Formation: 1.6.5.2.1
 $H_{10}Sn^*C_3$
 $H_{10}Sn^*C_4$
 $H_{10}Zn^*C_4$
 $H_{10}Zr^*C_8$
 $H_{11}Al^*C_4$
 $H_{11}As^*C_4$
 $H_{11}As^*C_8$
 $H_{11}As^*C_{12}$
 $H_{11}AsCl_2^*C_{13}$
 $H_{11}AsGe^*C_3$
 $H_{11}AsSi^*C_3$
 $H_{11}^*B_5$
 $H_{11}BrMg^*C_6$
 $H_{11}BrSn^*C_4$
 $H_{11}BrSn^*C_{12}$
 $H_{11}Br_3Ge^*C_5$
 $H_{11}Br_4O_3Rh_2^*C_{13}$
 $H_{11}ClFeO_2^*C_{10}$
 $H_{11}ClGe^*C_4$
 $H_{11}ClGe^*C_{12}$
 $H_{11}ClMg^*C_6$
 $H_{11}ClOZr^*C_{11}$
 $H_{11}ClO_2Si^*C_4$
 $H_{11}ClSi^*C_4$
 $H_{11}ClSi^*C_{12}$
 $H_{11}ClSn^*C_4$
 $H_{11}ClSn^*C_{12}$
 $H_{11}ClZr^*C_{10}$
 $H_{11}Cl_2P^*C_{13}$
 $H_{11}Cl_3GeO^*C_4$
 $H_{11}Cl_3GeO^*C_4$
 $H_{11}Cl_3Si^*C_5$
 $H_{11}CoN_2O_2^*C_9$
 $H_{11}FGe^*C_4$
 $H_{11}FSn^*C_4$
 $H_{11}FSn^*C_{12}$
 $H_{11}F_2OP^*C_8$
 $H_{11}F_6Fe_2O_4P^*C_{14}$
 $H_{11}F_6O_6PW_2^*C_{16}$
 $H_{11}F_7N_2PW^*C_{11}$
 $H_{11}K^*B_6$
 $H_{11}K^*B_9D_3$
 $H_{11}N^*C_4$
 $H_{11}N^*C_5$
 $H_{11}N^*C_8$
 $H_{11}N^*C_{12}$
 $H_{11}N^*C_{13}$
 $H_{11}NO_2^*C_6$
 $H_{11}NO_9Ru_3^*C_{14}$
 $H_{11}N_2OP^*C_8$
 $H_{11}NaZn^*C_{12}$
 $H_{11}NbO^*C_{11}$
 $H_{11}OP^*C_5$
 $H_{11}OP^*C_{12}$
 $H_{11}OTa^*C_{11}$
 $H_{11}O_2P^*C_4$
 $H_{11}O_2P^*C_5$
 $H_{11}O_2P^*C_8$
 $H_{11}O_2P^*C_{12}$
 $H_{11}O_2PS_2^*C_4$
 $H_{11}O_3P^*C_4$
 $H_{11}O_3P^*C_8$
 $H_{11}O_3P^*C_{12}$
 $H_{11}P^*C_4$
 $H_{11}P^*C_5$
 $H_{11}P^*C_8$
 $H_{11}P^*C_{10}$
 $H_{11}P^*C_{12}$
 $H_{11}PS^*C_4$
 $H_{11}PSi_2^*C_2$
 $H_{11}Re^*C_{10}$
 $H_{11}Sb^*C_4$
 $H_{11}Sb^*C_{12}$
 $H_{12}^*AlB_3$
 $H_{12}AlLi^*C_4$
 $H_{12}AlLiO_4^*C_4$
 $H_{12}^*Al_3Ga$
 $H_{12}AsN^*C_4$
 $H_{12}BF_4N_2O_2Re^*C_{14}$
 $H_{12}BGeK^*C_3$
 $H_{12}BN^*C_3$
 $H_{12}^*B_3Ga$
 $H_{12}^*B_6$
 $H_{12}^*B_8$
 $H_{12}^*B_{10}D_2$
 $H_{12}^*C_5$
 $H_{12}^*C_6$
 $H_{12}^*C_9$

$H_{12}C_{14}$
 $H_{12}ClFe_2O_4P^*C_{14}$
 $H_{12}ClNSi^*C_4$
 $H_{12}ClN_2P^*C_4$
 $H_{12}ClRe^*C_{10}$
 $H_{12}Cl_2Si^*C_9$
 $H_{12}CrF_9P_3^*C_8$
 $H_{12}CrO_3^*C_{12}$
 $H_{12}CrO_3P_2^*C_9$
 $H_{12}F_2Si_2^*C_4$
 $H_{12}F_5OP^*C_{14}$
 $H_{12}F_6N_2PW^*C_{11}$
 $H_{12}FeO^*C_9$
 $H_{12}Fe_2GeO_4^*C_{14}$
 $H_{12}Ge^*C_4$
 $H_{12}Ge^*C_{12}$
 $H_{12}GeO_8Sn^*C_8$
 $H_{12}Ge_2S_2^*C_4$
 $H_{12}Ge_3^*C_2$
 $H_{12}^*Ge_5$
 $H_{12}In^*Al_3$
 $H_{12}In^*B_3$
 $H_{12}IrNa_2O_6^*Cl_6$
 $H_{12}K^*B_5$
 $H_{12}K^*B_7$
 $H_{12}K_2P_4^*C_4$
 $H_{12}Li_2P_4^*C_4$
 $H_{12}Li_2Si_2^*C_4$
 $H_{12}MnNO_{12}Os_2^*C_{16}$
 $H_{12}Mo^*C_{10}$
 $H_{12}MoO_2^*C_{12}$
 $H_{12}MoO_5P_2^*C_9$
 $H_{12}MoP_2^*C_{10}$
 $H_{12}Mo_2O_8^*C_8$
 $H_{12}NO_3P^*C_6$
 $H_{12}NO_9Os_3^*C_{17}$
 $H_{12}NP^*C_4$
 $H_{12}NYb^*C_{10}$
 $H_{12}N_3^*B_3$
 $H_{12}NaZn^*B_3$
 $H_{12}Na_2O_6Os^*Cl_6$
 $H_{12}O^*C_5$
 $H_{12}OSi^*C_4$
 $H_{12}O_2Si^*C_4$
 $H_{12}O_2Sn^*C_4$
 $H_{12}O_3Ru_2^*C_{14}$
 $H_{12}O_4Rh^*C_{15}$
 $H_{12}Os_3^*C_{12}$
 $H_{12}P_2^*C_4$
 $H_{12}P_2^*C_{12}$
 $H_{12}P_2S_2^*C_4$
 $H_{12}Pb^*C_4$

$H_{12}Pb^*C_8$
 $H_{12}Si^*C_4$
 $H_{12}Si^*C_{12}$
 $H_{12}Si_2^*C_3$
 $H_{12}Si_2^*C_4$
 $H_{12}Si_3^*Ge_2$
 $H_{12}Si_4^*Ge$
 $H_{12}Si_5$
 $H_3Si(SiH_2)_3SiH_3$
 Formation: 1.6.3.2.1, 1.6.5.2.1
 $H_{12}Sn^*C_4$
 $H_{12}Sn^*C_4$
 $H_{12}Sn^*C_{12}$
 $H_{12}Tl^*Ga_3$
 $H_{12}W^*C_{10}$
 $H_{12}W^*C_{11}$
 $H_{12}Zr^*C_{10}$
 $H_{13}AsGe^*C_4$
 $H_{13}AsSi^*C_4$
 $H_{13}BF_4NO_3P^*C_6$
 $H_{13}BN_2^*C_4$
 $H_{13}BPb^*C_3$
 $H_{13}B_2Zr^*C_5$
 $H_{13}B_5^*C_2$
 $H_{13}^*B_{10}D$
 $H_{13}B_{10}Na^*C$
 $H_{13}Cl^*C_5$
 $H_{13}ClMoN_3O_6^*C_6$
 $H_{13}ClNO_6PS^*C_{18}$
 $H_{13}ClZr^*C_{11}$
 $H_{13}Cl_3Si^*C_6$
 $H_{13}Co^*C_8$
 $H_{13}Fe_3NO_{11}^*C_{15}$
 $H_{13}IW^*C_{11}$
 $H_{13}KZn_2^*C_4$
 $H_{13}NO_6P_2^*C_4$
 $H_{13}NO_{11}Ru_4^*C_{16}$
 $H_{13}N_2OP^*C_{10}$
 $H_{13}N_2O_2Re^*C_{14}$
 $H_{13}N_2PS^*C_{12}$
 $H_{13}Na^*B_{10}$
 $H_{13}Nb^*C_{10}$
 $H_{13}O_2P^*C_{13}$
 $H_{13}O_2P^*C_{14}$
 $H_{13}O_3P^*C_5$
 $H_{13}P^*C_6$
 $H_{13}P^*C_{14}$
 $H_{13}Rh^*C_{11}$
 $H_{13}Ta^*C_{10}$
 $H_{14}BNb^*C_{10}$
 $H_{14}^*B_{10}$
 $H_{14}B_{10}Li_2^*C_2$

- $H_{14}^*C_7$
 $H_{14}ClOP^*C_{10}$
 $H_{14}ClOP^*C_{14}$
 $H_{14}Cl_2Pb^*C_6$
 $H_{14}F_6PRh^*C_{11}$
 $H_{14}Fe_2O_3^*C_{15}$
 $H_{14}Ge^*C_5$
 $H_{14}GeP_2^*C_4$
 $H_{14}K^*B_9$
 $H_{14}NO_2P^*C_{10}$
 $H_{14}NO_3P^*C_{10}$
 $H_{14}NO_3P^*C_{11}$
 $H_{14}N_2^*C_5$
 $H_{14}N_2O^*C_{14}$
 $H_{14}N_2O_8Os_3^*C_{20}$
 $H_{14}N_2Si_5$
 $[(H_3Si)_2N]_2SiH_2$
 Formation: 1.6.3.2.2, 1.6.4.2.3
 $H_{14}OSi_2^*C_4$
 $H_{14}OZr^*C_{11}$
 $H_{14}O_3Ru_2^*C_{15}$
 $H_{14}O_3Ru_2^*C_{16}$
 $H_{14}P_2^*Ge_5$
 $H_{14}Si^*C_5$
 $H_{14}Si^*Ge_5$
 $H_{14}Si_2^*C_4$
 $H_{14}Si_6$
 $H_3Si(SiH_2)_4SiH_3$
 Formation: 1.6.3.2.1
 $H_{14}W^*C_{11}$
 $H_{14}W^*C_{12}$
 $H_{15}Al^*C_6$
 $H_{15}As^*C_6$
 $H_{15}As^*C_{14}$
 $H_{15}As^*C_{18}$
 $H_{15}AsGe^*C_9$
 $H_{15}AsSi^*C_5$
 $H_{15}AsSi^*C_9$
 $H_{15}AuMnO_3P_2^*C_{23}$
 $H_{15}B^*C_6$
 $H_{15}BCl_3OP^*C_{14}$
 $H_{15}BCl_3PS^*C_{14}$
 $H_{15}BDLi^*C_6$
 $H_{15}BF_4O_3Ru_2^*C_{16}$
 $H_{15}BGaN^*C_3$
 $H_{15}BO_2^*C_{18}$
 $H_{15}BO_3^*C_{18}$
 $H_{15}^*B_9$
 $H_{15}B_{10}N^*C$
 $H_{15}Bi^*C_{18}$
 $H_{15}BiCl_2^*C_{18}$
 $H_{15}BrGe^*C_6$
 $H_{15}BrGe^*C_{18}$
 $H_{15}BrMgSi^*C_{18}$
 $H_{15}BrNP^*C_{18}$
 $H_{15}ClGe^*C_6$
 $H_{15}ClGeMg^*C_6$
 $H_{15}ClGeMg^*C_{18}$
 $H_{15}ClIrOP^*C_{19}$
 $H_{15}ClPb^*C_6$
 $H_{15}ClSi^*C_6$
 $H_{15}ClSi^*C_{18}$
 $H_{15}ClSi_2^*C_5$
 $H_{15}ClSn^*C_6$
 $H_{15}ClSn^*C_{18}$
 $H_{15}Co^*C_{10}$
 $H_{15}CoN_2O_2^*C_{11}$
 $H_{15}DGe^*C_{18}$
 $H_{15}DSi^*C_{18}$
 $H_{15}DSn^*C_6$
 $H_{15}D_2N^*C_{11}$
 $H_{15}D_6Ni_3P_3^*C_{15}$
 $H_{15}FSi^*C_6$
 $H_{15}F_6MnO_3P_2^*C_{23}$
 $H_{15}F_6N_2PW^*C_{12}$
 $H_{15}Gd^*C_{15}$
 $H_{15}GeK^*C_6$
 $H_{15}GeK^*C_{18}$
 $H_{15}GeLi^*C_6$
 $H_{15}GeLi^*C_{18}$
 $H_{15}GeN^*C_5$
 $H_{15}GeNa^*C_6$
 $H_{15}GeNa^*C_{18}$
 $H_{15}IrO_2^*C_{12}$
 $H_{15}IrO_2^*C_{16}$
 $H_{15}KO_2Ru^*C_{12}$
 $H_{15}LiPb^*C_6$
 $H_{15}LiPb^*C_{18}$
 $H_{15}LiSn^*C_{18}$
 $H_{15}N^*B_{10}$
 $H_{15}N^*C_6$
 $H_{15}N^*C_{11}$
 $H_{15}N^*C_{14}$
 $H_{15}N^*C_{18}$
 $H_{15}NO^*C_{11}$
 $H_{15}NO_2^*C_6$
 $H_{15}NO_4^*C_{14}$
 $H_{15}NO_5^*C_{14}$
 $H_{15}NSn^*C_5$
 $H_{15}N_2O_2Re^*C_{15}$
 $H_{15}N_2P^*C_5$
 $H_{15}N_3P^*C_{13}$
 $H_{15}NaSn^*C_6$
 $H_{15}NaSn^*C_{18}$

$H_{15}Nd^*C_{15}$	$H_{16}NOP^*C_{11}$
$H_{15}OP^*C_{10}$	$H_{16}NOP^*C_{14}$
$H_{15}OP^*C_{19}$	$H_{16}NOPS^*C_{14}$
$H_{15}O_2P^*C_6$	$H_{16}NO_2P^*C_{10}$
$H_{15}O_2P^*C_{14}$	$H_{16}NO_2P^*C_{14}$
$H_{15}O_2P^*C_{18}$	$H_{16}NO_3P^*C_{12}$
$H_{15}O_2PW^*C_{10}$	$H_{16}NO_{11}Os_3P^*C_{29}$
$H_{15}O_2Rh^*C_{12}$	$H_{16}NP^*C_6$
$H_{15}O_3P^*C_6$	$H_{16}NP^*C_{18}$
$H_{15}O_3P^*C_{10}$	$H_{16}NPSSi^*C_5$
$H_{15}O_3P^*C_{12}$	$H_{16}N_2^*C_6$
$H_{15}O_3P^*C_{18}$	$H_{16}O^*C_7$
$H_{15}O_4P^*C_{12}$	$H_{16}OSi^*C_6$
$H_{15}P^*C_{14}$	$H_{16}O_2Os^*C_{12}$
$H_{15}P^*C_{18}$	$H_{16}O_2Ru^*C_{12}$
$H_{15}PSi^*C_5$	$H_{16}O_2Ru_2^*C_{15}$
$H_{15}PSi^*C_9$	$H_{16}O_2Si^*C_6$
$H_{15}Sb^*C_6$	$H_{16}O_2Sn^*C_6$
$H_{15}Sn^*C_{18}$	$H_{16}O_2Sn^*C_{14}$
$H_{15}Th_4$	$H_{16}O_3^*C_7$
Th_4H_{15}	$H_{16}O_5PV^*C_{23}$
Structure: 1.12.4.2	$H_{16}O_5Ru_2^*C_{17}$
$H_{16}AlLiZn_2^*C_4$	$H_{16}P_2^*C_{14}$
$H_{16}AlNa^*C_6$	$H_{16}Pb^*C_6$
$H_{16}BF_4IrO_2^*C_{12}$	$H_{16}Pb^*C_{18}$
$H_{16}BF_4MoN_3O_3^*C_9$	$H_{16}Si^*C_6$
$H_{16}BF_4N_2O_2Re^*C_{15}$	$H_{16}Si^*C_7$
$H_{16}BK^*C_{18}$	$H_{16}Si^*C_8$
$H_{16}BLi^*C_6$	$H_{16}Si^*C_{18}$
$H_{16}^*C_8$	$H_{16}Si_2^*C_4$
$H_{16}ClF_6N_4OOsP^*C_{25}$	$H_{16}Si_2^*C_5$
$H_{16}ClN^*C_6$	$H_{16}Si_3^*C_4$
$H_{16}Cl_2N_4O_5Ru^*C_{25}$	$H_{16}Sn^*C_6$
$H_{16}Cl_2Rh_2^*C_{14}$	$H_{16}Sn^*C_{18}$
$H_{16}CoO_3P^*C_{21}$	$H_{16}Ti^*C_{12}$
$H_{16}CoO_6P^*C_{21}$	$H_{16}W^*C_{18}$
$H_{16}CuP^*C_{18}$	$H_{17}Al^*C_7$
$H_{16}F_2GeSn^*C_6$	$H_{17}AsCl_2^*C_{18}$
$H_{16}F_2Ge_2^*C_6$	$H_{17}AsO^*C_{15}$
$H_{16}F_9IrN_4O_9S_3^*C_{27}$	$H_{17}AsO^*C_{19}$
$H_{16}FeO_4Si^*C_{22}$	$H_{17}Br^*C_8$
$H_{16}Fe_3N_2O_9^*C_{15}$	$H_{17}BrNP^*C_{18}$
$H_{16}Ge^*C_6$	$H_{17}ClNP^*C_{18}$
$H_{16}Ge^*C_7$	$H_{17}Cl_2Ir_2^*C_{20}$
$H_{16}Ge^*C_{18}$	$H_{17}F_6N_4OOsP^*C_{25}$
$H_{16}GeO^*C_{18}$	$H_{17}F_6N_4OPRu^*C_{21}$
$H_{16}Ge_2^*C_5$	$H_{17}MnO_5PN^*C_{22}$
$H_{16}Li_2^*B_4Cd$	$H_{17}NO_4^*C_{14}$
$H_{16}Li_2Zn^*B_4$	$H_{17}NO_5^*C_{14}$
$H_{16}MnO_2P^*C_{15}$	$H_{17}NP^*C_{11}$
$H_{16}MnO_4P^*C_{22}$	$H_{17}NSi^*C_6$
$H_{16}Mo^*C_{18}$	$H_{17}N_2PS^*C_{10}$

$H_{17}N_4P^*C_8$	$H_{19}Al^*C_8$
$H_{17}O_3P^*C_7$	$H_{19}As^*C_8$
$H_{17}O_3P^*C_{11}$	$H_{19}AsSi_2^*C_6$
$H_{17}P^*C_{19}$	$H_{19}BPb^*C_6$
$H_{17}P^*C_{24}$	$H_{19}B_2Li^*C_6$
$H_{17}PSn^*C_{10}$	$H_{19}ClSn^*C_8$
$H_{17}Ta^*C_{12}$	$H_{19}FSn^*C_8$
$H_{18}AlD^*C_3$	$H_{19}NPb^*C_7$
$H_{18}AlLiSi^*C_{18}$	$H_{19}NSi^*C_7$
$H_{18}Al_2^*C_6$	$H_{19}NSi_2^*C_6$
$H_{18}BD_3^*C_9$	$H_{19}NSn^*C_7$
$H_{18}BN_3^*C_{21}$	$H_{19}N_4P^*C_9$
$H_{18}BP^*C_{18}$	$H_{19}O_2P^*C_8$
$H_{18}BPSi^*C_5$	$H_{19}O_3P^*C_8$
$H_{18}B_2P_2^*C_4$	$H_{19}O_3Re^*C_{15}$
$H_{18}B_2Zr^*C_{10}$	$H_{19}P^*C_8$
$H_{18}^*B_{12}Cd$	$H_{19}PS^*C_8$
$H_{18}Be^*C_8$	$H_{19}PSi_2^*C_6$
$H_{18}^*C_8$	$H_{19}P_2Rh^*C_8$
$H_{18}ClIrOP_2^*C_7$	$H_{19}P_3^*C_8$
$H_{18}ClMnO_2Si^*C_{20}$	$H_{19}Sb^*C_8$
$H_{18}ClOP^*C_8$	$H_{19}Sb^*C_{10}$
$H_{18}ClP^*C_{19}$	$H_{20}BO_2Rh^*C_{18}$
$H_{18}ClSb^*C_8$	$H_{20}^*B_{14}$
$H_{18}Cl_2Pb^*C_8$	$H_{20}BrNiP^*C_{21}$
$H_{18}Cl_2Sn_2^*C_8$	$H_{20}^*C_{11}$
$H_{18}F_2NPSi_2^*C_6$	$H_{20}ClFeO_2P^*C_{25}$
$H_{18}Fe_3N_2O_9^*C_{20}$	$H_{20}ClMgN_2Ti_2^*C_{20}$
$H_{18}GeSi^*C_6$	$H_{20}Cl_2NPPt^*C_{25}$
$H_{18}Ge_2^*C_6$	$H_{20}Fe_4N_2O_{12}^*C_{20}$
$H_{18}HgSn_2^*C_6$	$H_{20}Fe_5N_2O_{12}^*C_{20}$
$H_{18}KP_3^*C_8$	$H_{20}GeSi_2^*C_6$
$H_{18}K_2P_2^*C_8$	$H_{20}K_2P_4^*C_8$
$H_{18}Li_2Si_2^*C_6$	$H_{20}LiO_2P^*C_{18}$
$H_{18}MoO_7PRE^*C_{26}$	$H_{20}Li_2P_4^*C_8$
$H_{18}NNaSi_2^*C_6$	$H_{20}NP^*C_8$
$H_{18}NO_3P^*C_{12}$	$H_{20}NP^*C_{16}$
$H_{18}NP^*C_{19}$	$H_{20}NP^*C_{17}$
$H_{18}NYb^*C_{15}$	$H_{20}NP^*C_{20}$
$H_{18}N_3P^*C_6$	$H_{20}NP^*C_{24}$
$H_{18}N_3P^*C_{18}$	$H_{20}NPSi_2^*C_6$
$H_{18}OOS^*C_{11}$	$H_{20}N_2O_8Ru_3^*C_{18}$
$H_{18}OSi_2^*C_6$	$H_{20}NbO_3^*C_{26}$
$H_{18}OSn^*C_8$	$H_{20}O_2PRE^*C_{25}$
$H_{18}O_2W^*C_{18}$	$H_{20}O_2Si^*C_8$
$H_{18}O_3P_2^*C_{11}$	$H_{20}O_2Si^*C_{16}$
$H_{18}O_3Ru_3^*C_{18}$	$H_{20}O_2Sn^*C_8$
$H_{18}Pb^*C_7$	$H_{20}O_3V^*C_{26}$
$H_{18}Si^*C_8$	$H_{20}O_4Si^*C_8$
$H_{18}Sn^*C_8$	$H_{20}O_4Sn^*C_8$
$H_{18}Ta^*C_{15}$	$H_{20}P_2^*C_{24}$
$H_{18}Zn^*C_8$	$H_{20}P_2Pt^*C_6$

$H_{20}P_2S_2^*C_8$	$H_{22}Co_3FeO_{14}P^*C_{20}$
$H_{20}Pb^*C_8$	$H_{22}F_6O_9Os_3P_2S^*C_{21}$
$H_{20}ReO_2P^*C_{25}$	$H_{22}Ge^*C_9$
$H_{20}Si_3^*C_6$	$H_{22}Ge^*C_{21}$
$H_{20}Sn^*C_8$	$H_{22}Ge_3^*C_7$
$H_{20}Sn^*C_{12}$	$H_{22}MnOP^*C_{25}$
$H_{21}AlO^*C_{18}$	$H_{22}Mn_2O_4P_2^*C_{26}$
$H_{21}B^*C_9$	$H_{22}N_2^*C_{13}$
$H_{21}BO_3^*C_9$	$H_{22}N_2O_{10}Ru_4^*C_{20}$
$H_{21}B_{10}N^*C_4$	$H_{22}N_2P_2S_2^*C_{24}$
$H_{21}ClGeMg^*C_9$	$H_{22}N_4^*C_9$
$H_{21}ClPb^*C_9$	$H_{22}N_4P_2^*C_{24}$
$H_{21}ClSn^*C_9$	$H_{22}NbP^*C_{18}$
$H_{21}CoO_6^*C_{15}$	$H_{22}OSi_2^*C_{24}$
$H_{21}CrO_2P^*C_{26}$	$H_{22}OSn^*C_{25}$
$H_{21}Cr_2NO_{10}^*C_{18}$	$H_{22}O_3Sn^*C_{10}$
$H_{21}DSi^*C_9$	$H_{22}P_2^*C_9$
$H_{21}FeO_3P^*C_{25}$	$H_{22}P_2Pt^*C_8$
$H_{21}GeK^*C_{21}$	$H_{22}P_4^*C_{24}$
$H_{21}GeLi^*C_{21}$	$H_{22}Pb^*C_9$
$H_{21}GeNa^*C_{21}$	$H_{22}Ru^*C_{16}$
$H_{21}GeP^*C_9$	$H_{22}Si^*C_9$
$H_{21}Ir^*C_{14}$	$H_{22}Si^*C_{25}$
$H_{21}IrNO_2P^*C_{28}$	$H_{22}Si_2^*C_8$
$H_{21}MoO_3P_3^*C_{12}$	$H_{22}Sn^*C_9$
$H_{21}MoO_6^*C_{15}$	$H_{22}Sn^*C_{12}$
$H_{21}NOPRe^*C_{23}$	$H_{23}As^*C_{12}$
$H_{21}NOSi^*C_{13}$	$H_{23}B_3CuP^*C_{18}$
$H_{21}NO_3PRe^*C_{24}$	$H_{23}Cl_3NP_2Re^*C_{12}$
$H_{21}NO_6P_2^*C_8$	$H_{23}CoP_2^*C_{11}$
$H_{21}NO_9Re_2^*C_{17}$	$H_{23}Co_2F_6P_3^*C_{14}$
$H_{21}NSSi^*C_9$	$H_{23}DN_3P_3^*C_{25}$
$H_{21}NSn^*C_8$	$H_{23}GeP^*C_9$
$H_{21}N_6P_3^*C_6$	$H_{23}IrP_2^*C_6$
$H_{21}NiP^*C_{23}$	$H_{23}MnOP^*C_{25}$
$H_{21}Ni_3P_3^*C_{15}$	$H_{23}MnO_2Si^*C_{25}$
$H_{21}ORhSi^*C_{24}$	$H_{23}NSi_2^*C_{12}$
$H_{21}O_2P^*C_{18}$	$H_{23}N_2Ti_2^*C_{20}$
$H_{21}O_2PSn^*C_{12}$	$H_{23}N_3P_2^*C_{24}$
$H_{21}O_2ReSi^*C_{25}$	$H_{23}NiPSi_2^*C_{11}$
$H_{21}O_3P^*C_9$	$H_{23}O_2P^*C_{12}$
$H_{21}O_9Os_3PS^*C_{21}$	$H_{23}O_3P^*C_{12}$
$H_{21}P_2Ta^*C_6$	$H_{23}P^*C_{12}$
$H_{22}BKO_3^*C_9$	$H_{23}PPtS_2^*C_{21}$
$H_{22}^*C_{28}$	$H_{23}PSi_2^*C_{12}$
$H_{22}ClGeP^*C_9$	$H_{23}Sb^*C_{12}$
$H_{22}ClIrNO_2P^*C_{28}$	$H_{24}AuClN_3P_3^*C_{25}$
$H_{22}ClSb^*C_{12}$	$H_{24}B_3P_3^*C_6$
$H_{22}Cl_2N_2Ti_2^*C_{20}$	$H_{24}Cl_2Ir_2^*C_{16}$
$H_{22}Cl_2Pb^*C_{12}$	$H_{24}Cl_2Mg_2NO_5Ti^*C_{13}$
$H_{22}Cl_4P_2W^*C_{16}$	$H_{24}Cl_2Mg_2NO_5V^*C_{13}$
$H_{22}Co_2P_2^*C_{14}$	$H_{24}Cl_4Ni_2^*C_{16}$

- $H_{24}CoF_6P_3^*C_{11}$
 $H_{24}D_3IrOP_2^*C_{27}$
 $H_{24}F_6P_4Rh^*C_{26}$
 $H_{24}Li_2Si_4^*C_8$
 $H_{24}MoN_4^*C_8$
 $H_{24}Mo_2N_4O_4^*C_{24}$
 $H_{24}NPSSi_2^*C_8$
 $H_{24}N_2^*C_{10}$
 $H_{24}N_3P_3^*C_{25}$
 $H_{24}N_4^*C_{10}$
 $H_{24}O_3P_2^*C_{18}$
 $H_{24}O_6P_2^*C_{10}$
 $H_{24}P_2^*C_{14}$
 $H_{24}Pt^*C_{16}$
 $H_{24}Si_2^*C_{21}$
 $H_{24}Si_3^*C_9$
 $H_{24}Sn^*C_{14}$
 $H_{24}Zr^*C_{17}$
 $H_{25}BPb^*C_9$
 $H_{25}ClGeTi^*C_{28}$
 $H_{25}ClMo^*C_{33}$
 $H_{25}GeP^*C_{10}$
 $H_{25}GeP^*C_{18}$
 $H_{25}IrOP_2^*C_{27}$
 $H_{25}LiOSi^*C_{31}$
 $H_{25}NSn^*C_{10}$
 $H_{25}NSn^*C_{22}$
 $H_{25}N_4P^*C_{12}$
 $H_{25}Na_3O_{17}P_4$
 $Na_3[HP_2O_3] \cdot 12 H_2O$
 Formation: 1.5.3.2.1
 $H_{25}PSn^*C_{18}$
 $H_{25}PSn^*C_{30}$
 $H_{25}P_5^*C_{30}$
 $H_{26}BCuO_2P_2^*C_{26}$
 $H_{26}BF_4OP_2Pt^*C_{22}$
 $H_{26}ClMoP^*C_{27}$
 $H_{26}Cl_2NOPPt^*C_{27}$
 $H_{26}Cl_4Ir_2^*C_{16}$
 $H_{26}Cl_4MoP_2^*C_{26}$
 $H_{26}IrP^*C_{13}$
 $H_{26}Mo^*C_{33}$
 $H_{26}N_2Sn^*C_{10}$
 $H_{26}N_4^*C_{11}$
 $H_{26}OSi^*C_{11}$
 $H_{26}OSi^*C_{31}$
 $H_{26}O_4Si^*C_{11}$
 $H_{26}Si_4^*C_8$
 $H_{26}Sn_2^*C_{10}$
 $H_{26}Sn_2^*C_{18}$
 $H_{27}Al^*C_{12}$
 $H_{27}Al^*C_{16}$
 $H_{27}AsSi_2^*C_{10}$
 $H_{27}AsSi_3^*C_9$
 $H_{27}BN_2Sn^*C_{10}$
 $H_{27}BiGe_3^*C_9$
 $H_{27}ClPb^*C_{12}$
 $H_{27}ClSn^*C_{12}$
 $H_{27}Cl_4P_3W^*C_9$
 $H_{27}Co_3FeNO_{12}P^*C_{22}$
 $H_{27}DSn^*C_{12}$
 $H_{27}IrOP_2^*C_{27}$
 $H_{27}LiSn^*C_{12}$
 $H_{27}NPSSi^*C_{11}$
 $H_{27}NPSi_3^*C_9$
 $H_{27}N_2PSSi_2^*C_{10}$
 $H_{27}N_2PSi_2^*C_{10}$
 $H_{27}N_2PSi_3^*C_9$
 $H_{27}NaSn^*C_{12}$
 $H_{27}OPSi^*C_{11}$
 $H_{27}O_2PSn^*C_{15}$
 $H_{27}O_3P^*C_{12}$
 $H_{27}PPt^*C_{16}$
 $H_{27}P_3Si^*C_{11}$
 $H_{27}SbSn_3^*C_9$
 $H_{28}AlLiO_3^*C_{12}$
 $H_{28}BCuP_2^*C_{26}$
 $H_{28}BK^*C_{12}$
 $H_{28}Cl_2Ge_2^*C_{12}$
 $H_{28}Cl_2Si_2^*C_{12}$
 $H_{28}Cl_4IrP_3^*C_9$
 $H_{28}Ge^*C_{12}$
 $H_{28}MoN_4P_3^*C_{28}$
 $H_{28}NP^*C_{12}$
 $H_{28}N_4Zn_2^*C_{10}$
 $H_{28}O_2Sn^*C_{13}$
 $H_{28}O_4PSi^*C_{16}$
 $H_{28}O_{10}Os_3^*C_{26}$
 $H_{28}PRh^*C_{14}$
 $H_{28}P_2Pt^*C_{27}$
 $H_{28}Pb^*C_{12}$
 $H_{28}Si_2^*C_{31}$
 $H_{28}Sn^*C_{12}$
 $H_{28}Sn_2^*C_{18}$
 $H_{29}ClN_4O_4Rh^*C_{26}$
 $H_{29}NO_6P_2^*C_{12}$
 $H_{29}N_2PSi_3^*C_9$
 $H_{29}OP^*C_{14}$
 $H_{29}O_2PS_2Si^*C_{12}$
 $H_{29}PPtS_3^*C_{24}$
 $H_{29}P_2Re^*C_{16}$
 $H_{30}As_2ClIrO^*C_{37}$
 $H_{30}AuGeP^*C_{36}$
 $H_{30}BClF_4OP_2Pt^*C_{13}$

$H_{30}B_{10}IrO_3P^*C_{29}$
 $H_{30}BrIrOP_2^*C_{37}$
 $H_{30}BrIrO_7P_2^*C_{37}$
 $H_{30}CdGe_2^*C_{12}$
 $H_{30}ClIrOP_2^*C_{13}$
 $H_{30}ClIrOP_2^*C_{37}$
 $H_{30}ClIrO_7P_2^*C_{37}$
 $H_{30}ClIrO_7P_2^*C_{39}$
 $H_{30}ClIrP_2^*C_{26}$
 $H_{30}ClIrP_2^*C_{37}$
 $H_{30}ClNO_2OsP_2^*C_{37}$
 $H_{30}ClOP_2Rh^*C_{37}$
 $H_{30}Cl_2P_2Pt^*C_{12}$
 $H_{30}Cl_3OP_2Re^*C_{20}$
 $H_{30}Cl_4P_2W^*C_{28}$
 $H_{30}Co_2N_6O_4^*C_{34}$
 $H_{30}F_6IrO_3P_3^*C_{39}$
 $H_{30}F_8O_2Pt_2^*C_{32}$
 $H_{30}Fe_5N_6O_{13}^*C_{43}$
 $H_{30}GeSi^*C_{20}$
 $H_{30}Ge_2^*C_{12}$
 $H_{30}Ge_2O^*C_{36}$
 $H_{30}HgSn_2^*C_{12}$
 $H_{30}IlrOP_2^*C_{37}$
 $H_{30}IlrO_7P_2^*C_{37}$
 $H_{30}Li_2Si_5^*C_{10}$
 $H_{30}MgSn_2^*C_{36}$
 $H_{30}NP_2Re^*C_{12}$
 $H_{30}N_2O_2OsP_2^*C_{36}$
 $H_{30}N_2Sn^*C_{12}$
 $H_{30}N_2Ti^*C_{20}$
 $H_{30}N_2U^*C_{18}$
 $H_{30}N_3P^*C_{12}$
 $H_{30}N_4O_4PRh^*C_{26}$
 $H_{30}N_4O_4Rh^*C_{26}$
 $H_{30}N_6P_2Pt^*C_{36}$
 $H_{30}Ni^*C_{20}$
 $H_{30}OP^*C_{14}$
 $H_{30}O_2Os_2^*C_{22}$
 $H_{30}O_2Pb^*C_{14}$
 $H_{30}O_2Zr^*C_{22}$
 $H_{30}O_3OsP_2^*C_{39}$
 $H_{30}P_2Pt^*C_{12}$
 $H_{30}Pb^*C_{14}$
 $H_{30}Si_2^*C_{12}$
 $H_{30}Si_2^*C_{36}$
 $H_{30}Sn_2^*C_{12}$
 $H_{30}Sn_2^*C_{36}$
 $H_{31}AuGeP^*C_{36}$
 $H_{31}BF_4O_3Rh_2^*C_{23}$
 $H_{31}BF_{12}O_2Pt_2^*C_{32}$
 $H_{31}BPb^*C_{12}$
 $H_{31}B_{10}NSi_2^*C_7$
 $H_{31}BrP_2Pt^*C_{12}$
 $H_{31}ClIrNP_2^*C_{37}$
 $H_{31}ClO_2P_2Pt^*C_{13}$
 $H_{31}ClO_7Os_2P_2^*C_{39}$
 $H_{31}ClPRhSi^*C_{36}$
 $H_{31}ClP_2Pt^*C_{12}$
 $H_{31}ClP_2Pt^*C_{36}$
 $H_{31}Cl_2IrOP_2^*C_{37}$
 $H_{31}Cl_2NO_2OsP_2^*C_{37}$
 $H_{31}D_2IrOP_2^*C_{37}$
 $H_{31}F_6NP_2Pt^*C_{39}$
 $H_{31}FeNO_2P_2^*C_{40}$
 $H_{31}Fe_2NO_8P_2^*C_{44}$
 $H_{31}IP_2Pt^*C_{12}$
 $H_{31}IrOP_2^*C_{37}$
 $H_{31}IrO_2P_2^*C_{38}$
 $H_{31}NO_{18}P_2Ru_6^*C_{54}$
 $H_{31}NP_2Pt^*C_{37}$
 $H_{31}N_2OPSSi^*C_{12}$
 $H_{31}N_2OPSSi_2^*C_{11}$
 $H_{31}PPt^*C_{18}$
 $H_{31}P_3Si^*C_{12}$
 $H_{32}B_2CoF_8P_3^*C_{14}$
 $H_{32}B_{10}IrO_2P^*C_{28}$
 $H_{32}B_{10}IrO_3P^*C_{29}$
 $H_{32}ClIrOP_2^*C_{37}$
 $H_{32}ClIrOP_4^*C_{13}$
 $H_{32}ClIrSi^*C_{16}$
 $H_{32}ClP_2IrS^*C_{36}$
 $H_{32}ClP_2RhS^*C_{36}$
 $H_{32}Cl_2N_2O_2OsP_2^*C_{36}$
 $H_{32}Cl_2P_4Ta^*C_{12}$
 $H_{32}F_{12}IrN_4P_3^*C_{42}$
 $H_{32}GeSi^*C_{13}$
 $H_{32}Ge_2^*C_{13}$
 $H_{32}K_2Zn_3^*B_8$
 $H_{32}NP_3^*C_{31}$
 $H_{32}OZr^*C_{21}$
 $H_{32}O_2Os_2^*C_{22}$
 $H_{32}O_2P_2Ru^*C_{38}$
 $H_{32}P_2Pt^*C_{12}$
 $H_{32}P_2PtS^*C_{36}$
 $H_{32}Si_5^*C_{10}$
 $H_{32}Zr^*C_{20}$
 $H_{33}B_{10}IrNOP^*C_{29}$
 $H_{33}ClGeMg^*C_{18}$
 $H_{33}ClP_2Ru^*C_{16}$
 $H_{33}Cl_3IrNOP_2^*C_{36}$
 $H_{33}Cl_3P_3Re^*C_{24}$
 $H_{33}Cl_4P_3W^*C_{24}$
 $H_{33}CoP_2^*C_{16}$

- $H_{33}F_6O_3PRh_2 * C_{20}$
 $H_{33}IrOP_2 * C_{37}$
 $H_{33}IrO_4P_2 * C_{40}$
 $H_{33}LiPb * C_{18}$
 $H_{33}NPSi * C_{26}$
 $H_{33}NSn * C_{14}$
 $H_{33}N_3Sn * C_{13}$
 $H_{33}PPt * C_{15}$
 $H_{33}P_2Re * C_{26}$
 $H_{33}P_3W * C_9$
 $H_{34}BCuP_2 * C_{36}$
 $H_{34}B_{12}O_2Zn * C_8$
 $H_{34}CoF_6P_3 * C_{16}$
 $H_{34}Ge * C_{18}$
 $H_{34}Ge * C_{20}$
 $H_{34}GeO_2 * C_{16}$
 $H_{34}OPtSP_2 * C_{38}$
 $H_{34}OZR * C_{21}$
 $H_{34}O_2P_2Ru * C_{36}$
 $H_{34}P_2Pt * C_{14}$
 $H_{34}P_2Pt * C_{22}$
 $H_{34}P_2Ru * C_{16}$
 $H_{34}Pb * C_{18}$
 $H_{35}B_{10}IrNOP * C_{29}$
 $H_{35}B_{10}IrNOP * C_{34}$
 $H_{35}Br_2MoN_2P_3 * C_{24}$
 $H_{35}Br_2N_2P_3W * C_{24}$
 $H_{35}ClN_2P_2Pt * C_{18}$
 $H_{35}ClP_2Pt * C_{14}$
 $H_{35}ClP_2Ru * C_{41}$
 $H_{35}IrP_2 * C_{36}$
 $H_{35}N_3Sn * C_{14}$
 $H_{35}PPt * C_{16}$
 $H_{35}PRu * C_{30}$
 $H_{36}As_4O_6Ru_3 * C_{44}$
 $H_{36}BF_4IrO_2P_2 * C_{36}$
 $H_{36}B_2CuN_2P_2 * C_{38}$
 $H_{36}Br_2ClN_2P_3W * C_{24}$
 $H_{36}ClNOP_2Pt * C_{19}$
 $H_{36}ClNOP_2Pt * C_{43}$
 $H_{36}ClNP_2Pt * C_{18}$
 $H_{36}ClNP_2Pt * C_{42}$
 $H_{36}ClP_3Si_4 * C_{12}$
 $H_{36}Cl_2N_2P_2Pt * C_{18}$
 $H_{36}Co_7Fe_2O_3 * C_{42}$
 $H_{36}F_6IrP_5 * C_{12}$
 $H_{36}F_6P_2Ru * C_{30}$
 $H_{36}FeP_2 * C_{43}$
 $H_{36}FeP_4 * C_{12}$
 $H_{36}Fe_3O_8Sb_2 * C_{45}$
 $H_{36}Ge_6P_4 * C_{12}$
 $H_{36}Ir_2N_6O_2P_2S_2 * C_{16}$
 $H_{36}Ir_2O_2P_2S_2 * C_{16}$
 $H_{36}Ir_2O_8P_2S_2 * C_{16}$
 $H_{36}Li_2Si_6 * C_{12}$
 $H_{36}NO_3V * C_{44}$
 $H_{36}N_2Si_2Sn * C_{14}$
 $H_{36}N_2Si_4Sn * C_{12}$
 $H_{36}N_4Si_4 * C_{12}$
 $H_{36}N_6W_2 * C_{12}$
 $H_{36}P_2Pt * C_{18}$
 $H_{36}P_2Ru * C_{41}$
 $H_{36}P_2S_2 * C_{16}$
 $H_{36}P_4Pd * C_{12}$
 $H_{36}P_4Si_4 * C_{12}$
 $H_{36}Si_6 * C_{12}$
 $H_{36}ZrO_4 * C_{16}$
 $H_{37}BCuP_3 * C_{24}$
 $H_{37}B_{10}IrNOP * C_{34}$
 $H_{37}B_{10}IrOP_2 * C_{29}$
 $H_{37}ClFeP_2 * C_{43}$
 $H_{37}ClIrP_3 * C_{36}$
 $H_{37}ClP_2Pt * C_{15}$
 $H_{37}ClSi_6 * C_{12}$
 $H_{37}Cl_3NP_2Re * C_{43}$
 $H_{37}NO_{11}Ru_3 * C_{27}$
 $H_{37}OP_2Rh * C_{40}$
 $H_{37}O_3P_3Pt * C_{42}$
 $H_{37}P_2Re * C_{20}$
 $H_{37}P_2Re * C_{36}$
 $H_{38}AgB_3P_2 * C_{36}$
 $H_{38}BF_4IrN_2P_2 * C_{40}$
 $H_{38}BF_4OPPt * C_{17}$
 $H_{38}B_3CuP_2 * C_{36}$
 $H_{38}B_3IrOP_2 * C_{37}$
 $H_{38}B_3CuP_2 * C_{36}$
 $H_{38}ClIrOP_2 * C_{33}$
 $H_{38}Cl_2NP_2Re * C_{43}$
 $H_{38}Cl_6P_4Ta_2 * C_{12}$
 $H_{38}F_6IrOP_5 * C_{13}$
 $H_{38}F_6P_3Ir * C_{34}$
 $H_{38}Ir_2N_6O_2P_2S_2 * C_{16}$
 $H_{38}Ir_2O_2P_2S_2 * C_{16}$
 $H_{38}Ir_2O_8P_2S_2 * C_{16}$
 $H_{38}MoP_2 * C_{42}$
 $H_{38}N_2Sn * C_{19}$
 $H_{38}OsP_4 * C_{12}$
 $H_{38}P_3Re * C_{24}$
 $H_{38}P_4Si_2 * C_{30}$
 $H_{38}Si_4Sn * C_{14}$
 $H_{38}Si_6 * C_{12}$
 $H_{38}Sn_2 * C_{16}$
 $H_{39}Al * C_{19}$
 $H_{39}BF_4OP_2Pt * C_{19}$

$H_{39}BNO_2P_2V^*C_{43}$	$H_{44}BF_4IrO_2P_2^*C_{42}$
$H_{39}B_6CuP_2^*C_{36}$	$H_{44}ClP_2Rh^*C_{21}$
$H_{39}B_{10}IrOP_2^*C_{29}$	$H_{44}Cl_2GeP_2Pt^*C$
$H_{39}B_{10}IrOP_2^*C_{30}$	$H_{44}Cl_2P_4Pt_2^*C_{50}$
$H_{39}B_{10}IrOP_2^*C_{35}$	$H_{44}FeIrO_4P_3^*C_{52}$
$H_{39}Br_2N_2P_3W^*C_{27}$	$H_{44}K_2P_4^*C_{24}$
$H_{39}ClIrP_3^*C_{36}$	$H_{44}Li_2P_4^*C_{24}$
$H_{39}ClP_4Ru^*C_{13}$	$H_{44}MoN_4P_4^*C_{32}$
$H_{39}ClSi^*C_{18}$	$H_{44}MoO_3Si_4Sn^*C_{22}$
$H_{39}NSn^*C_{25}$	$H_{44}N_4P_4W^*C_{32}$
$H_{39}P_3W^*C_{24}$	$H_{44}OP_2Pt^*C_{18}$
$H_{40}BF_4IrO_2P_2^*C_{38}$	$H_{44}O_2P_4Pt_2^*C_{52}$
$H_{40}Br_4Ni_2^*C_{56}$	$H_{44}O_8P_4Ru_3^*C_{58}$
$H_{40}Cl_4Pd_2^*C_{56}$	$H_{44}P_2Pt^*C_{18}$
$H_{40}Cr_2N_2O_{10}^*C_{26}$	$H_{44}P_2Pt^*C_{19}$
$H_{40}FeIrO_4P_3^*C_{52}$	$H_{44}P_2Pt^*C_{27}$
$H_{40}FeIrO_5P_3^*C_{53}$	$H_{44}P_2RuSi^*C_{20}$
$H_{40}N_2Sn_2O_4^*C_{18}$	$H_{44}P_3Re^*C_{39}$
$H_{40}N_4U^*C_{16}$	$H_{45}B_{10}IrOP_2^*C_{40}$
$H_{40}P_2Pt^*C_{50}$	$H_{45}B_{10}IrOP_2^*C_{45}$
$H_{40}P_4Ru^*C_{13}$	$H_{45}BiGe_3^*C_{18}$
$H_{40}Si^*C_{18}$	$H_{45}BiSi_3^*C_{18}$
$H_{40}Si_4^*C_{48}$	$H_{45}ClCuP_3^*C_{54}$
$H_{41}B_{10}IrOP_2^*C_{30}$	$H_{45}ClIrP_3^*C_{54}$
$H_{41}B_{10}IrOP_2^*C_{35}$	$H_{45}ClP_3Rh^*C_{54}$
$H_{41}B_{10}IrOP_2^*C_{39}$	$H_{45}ClRh^*C_{54}$
$H_{41}B_{10}IrOP_3^*C_{39}$	$H_{45}Cl_2F_6P_5Pt_2^*C_{50}$
$H_{41}ClCoN_4O_4^*C_{20}$	$H_{45}Cl_2P_3Rh^*C_{42}$
$H_{41}FeO_2P^*C_{26}$	$H_{45}Cl_2P_3Ru^*C_{54}$
$H_{42}BF_4FeO_2P^*C_{26}$	$H_{45}Cl_3IrP_3^*C_{18}$
$H_{42}BF_4IrP_2^*C_{44}$	$H_{45}Cl_3P_3Re^*C_{30}$
$H_{42}BrIrOP_2^*C_{19}$	$H_{45}CoP_4^*C_{32}$
$H_{42}ClIrOP_2^*C_{19}$	$H_{45}F_6OP_5Pt_2^*C_{51}$
$H_{42}ClIrOP_2^*C_{43}$	$H_{45}FeN_5O_5^*C_{25}$
$H_{42}CoN_4O_4^*C_{20}$	$H_{45}FeO_{15}P_5^*C_{15}$
$H_{42}CoN_4O_4P^*C_{20}$	$H_{45}Ge_2NSn^*C_{42}$
$H_{42}FeIrO_5P_3^*C_{53}$	$H_{45}Ge_3Sb^*C_{18}$
$H_{42}HgSn_2^*C_{18}$	$H_{45}Ge_3Tl^*C_{18}$
$H_{42}IIrOP_2^*C_{19}$	$H_{45}Ge_4Li^*C_{54}$
$H_{42}OWZr^*C_{31}$	$H_{45}IrNOP_3^*C_{54}$
$H_{42}P_2Pt^*C_{18}$	$H_{45}IrP_2^*C_{45}$
$H_{43}As_4O_7Ru_3^*C_{57}$	$H_{45}OP_4Pt_2^*C_{51}$
$H_{43}B_{10}IrOP_2^*C_{35}$	$H_{45}O_2OsP_3^*C_{56}$
$H_{43}B_{10}IrOP_2^*C_{39}$	$H_{45}O_3P_2Rh^*C_{19}$
$H_{43}B_{10}IrOP_2^*C_{40}$	$H_{45}P_2Rh^*C_{18}$
$H_{43}Cl_2OsP_3^*C_{30}$	$H_{45}P_3Pt^*C_{18}$
$H_{43}F_3O_2P_2Pd^*C_{20}$	$H_{45}P_3Pt^*C_{54}$
$H_{43}IrP_2^*C_{44}$	$H_{46}BF_4FeN_5^*C_{25}$
$H_{43}P_2Re^*C_{42}$	$H_{46}BrIrP_2^*C_{21}$
$H_{43}P_2Rh^*C_{18}$	$H_{46}ClIrP_2^*C_{21}$
$H_{44}As_4O_8Ru_3^*C_{58}$	$H_{46}ClOOSp_3^*C_{55}$
$H_{44}BF_4IrO_2P_2^*C_{40}$	$H_{46}ClOP_3Ru^*C_{31}$

- $H_{46}ClP_3Rh^*C_{21}$
 $H_{46}ClP_3Ru^*C_{54}$
 $H_{46}Cl_2IrP_3^*C_{18}$
 $H_{46}CoN_2P_3^*C_{54}$
 $H_{46}F_6FeO_{15}P_6^*C_{15}$
 $H_{46}Ge_4^*C_{54}$
 $H_{46}IrOP_3^*C_{55}$
 $H_{46}INOP_3Ru^*C_{54}$
 $H_{46}N_3PSi_4^*C_{10}$
 $H_{46}N_3PSi_5^*C_{15}$
 $H_{46}Ni_2P_2Si_4^*C_{22}$
 $H_{46}OP_3Rh^*C_{55}$
 $H_{46}O_6P_4Ru_3^*C_{56}$
 $H_{46}P_2Pd^*C_{28}$
 $H_{46}P_2Pt^*C_{28}$
 $H_{46}P_3Rh^*C_{54}$
 $H_{47}AgBO_2P_3^*C_{42}$
 $H_{47}B_2F_8FeN_5O^*C_{25}$
 $H_{47}B_{10}IrOP_2^*C_{45}$
 $H_{47}ClNP_2Rh^*C_{47}$
 $H_{47}ClP_2Pt^*C_{28}$
 $H_{47}ClP_3Rh^*C_{54}$
 $H_{47}F_6O_6P_3Pt_6^*C_{58}$
 $H_{47}N_2P_3Ru^*C_{54}$
 $H_{47}OOsP_3^*C_{55}$
 $H_{47}OP_3Ru^*C_{55}$
 $H_{47}P_4Pt_2^*C_{50}$
 $H_{47}P_4Re^*C_{32}$
 $H_{48}BCuNP_3^*C_{55}$
 $H_{48}BF_4IrO_2P_2^*C_{42}$
 $H_{48}BF_4IrO_2P_2^*C_{44}$
 $H_{48}ClIrP_2^*C_{22}$
 $H_{48}ClIrP_4^*C_{54}$
 $H_{48}Cl_2FeP_3^*C_{20}$
 $H_{48}Cl_2FeP_4^*C_{52}$
 $H_{48}CoP_3^*C_{54}$
 $H_{48}F_6OPRh_3^*C_{30}$
 $H_{48}IrP_3^*C_{54}$
 $H_{48}Ir_2O_2P_2S_2^*C_{46}$
 $H_{48}MoN_4P_4^*C_{52}$
 $H_{48}N_4P_2W^*C_{52}$
 $H_{48}N_4P_4W^*C_{52}$
 $H_{48}NiPi_4^*C_{52}$
 $H_{48}P_2PtSn_2^*C_{42}$
 $H_{49}Br_2MoNP_4^*C_{52}$
 $H_{49}ClFeP_4^*C_{52}$
 $H_{49}ClNP_2Rh^*C_{47}$
 $H_{49}ClN_2P_2Rh^*C_{46}$
 $H_{49}ClRhP_4^*C_{20}$
 $H_{49}F_6P_4Pt_2S^*C_{51}$
 $H_{49}IrP_2^*C_{21}$
 $H_{49}O_2P_3Ru^*C_{56}$
 $H_{49}OsP_3^*C_{54}$
 $H_{50}Br_2MoN_2P_4^*C_{52}$
 $H_{50}Br_2N_2P_4W^*C_{52}$
 $H_{50}ClP_2RhS^*C_{46}$
 $H_{50}FeP_4^*C_{52}$
 $H_{50}Ir_2O_2P_2S_2^*C_{46}$
 $H_{50}P_3Re^*C_{30}$
 $H_{50}P_3Re^*C_{54}$
 $H_{50}P_4Ru^*C_{52}$
 $H_{50}Si_5^*C_{60}$
 $H_{51}AgBO_2P_3^*C_{56}$
 $H_{51}BCuO_2P_3^*C_{56}$
 $H_{51}B_{30}ClIrP_3^*C_{12}$
 $H_{51}BrN_2P_4W^*C_{52}$
 $H_{51}ClN_2P_2Rh^*C_{46}$
 $H_{51}Cu_6P_3^*C_{54}$
 $H_{51}IMoN_2P_4^*C_{53}$
 $H_{51}IrP_2^*C_{22}$
 $H_{51}MoN_2O_4P_4S^*C_{52}$
 $H_{51}MoP_3^*C_{24}$
 $H_{52}BF_4IMoN_2P_4^*C_{53}$
 $H_{52}BF_4IrO_2P_2^*C_{44}$
 $H_{52}BF_4P_4Rh^*C_{54}$
 $H_{52}BrClN_2P_4W^*C_{53}$
 $H_{52}ClP_2RhS^*C_{46}$
 $H_{52}F_6MoP_4^*C_{24}$
 $H_{52}MoN_4P_4^*C_{52}$
 $H_{52}MoP_4^*C_{52}$
 $H_{52}N_4P_4W^*C_{52}$
 $H_{52}P_2Pt^*C_{34}$
 $H_{52}P_4Pd^*C_{52}$
 $H_{53}AgB_3P_3^*C_{54}$
 $H_{53}B_{10}Cl_2CuN_2^*C_{16}$
 $H_{53}F_{12}MoP_5^*C_{24}$
 $H_{54}BF_4P_4Rh^*C_{54}$
 $H_{54}ClF_6P_5Pt_2^*C_{54}$
 $H_{54}ClN_3Si_6Th^*C_{18}$
 $H_{54}Ge_2P_2Pt^*C_{33}$
 $H_{54}HgSn_2^*C_{24}$
 $H_{54}OSn_2^*C_{24}$
 $H_{54}P_2Pd^*C_{24}$
 $H_{54}P_2Pt^*C_{24}$
 $H_{54}P_4Ru^*C_{52}$
 $H_{54}P_4Ru^*C_{54}$
 $H_{55}As_2ClPt^*C_{24}$
 $H_{55}As_2F_3O_2Pt^*C_{26}$
 $H_{55}DGeNiP_3^*C_{66}$
 $H_{55}F_6P_5Pt_2^*C_{54}$
 $H_{55}Ge_2N^*C_{24}$
 $H_{55}N_2P_2Rh^*C_{24}$
 $H_{55}N_3Si_6Th^*C_{18}$
 $H_{55}P_4Re^*C_{52}$

$H_{56}As_2Pt^*C_{24}$
 $H_{56}Cl_2Ir_2^*C_{32}$
 $H_{56}GeNiP_3^*C_{66}$
 $H_{56}MoO_2P_4^*C_{57}$
 $H_{56}MoP_4^*C_{52}$
 $H_{56}OP_6Ru_2^*C_{18}$
 $H_{56}P_4W^*C_{52}$
 $H_{57}BrMoN_2P_4^*C_{56}$
 $H_{57}F_6P_5W^*C_{52}$
 $H_{57}P_2Rh^*C_{24}$
 $H_{58}FeP_2^*C_{40}$
 $H_{58}MoN_2P_4^*C_{57}$
 $H_{58}Mo_2P_6^*C_{18}$
 $H_{58}P_2PtSn^*C_{27}$
 $H_{58}P_4Ru^*C_{56}$
 $H_{60}Cl_2O_{12}P_4Ru^*C_{24}$
 $H_{60}GeP_2Pd^*C_{48}$
 $H_{60}Ge_2P_2Pd^*C_{48}$
 $H_{60}Ge_2P_2Pt^*C_{48}$
 $H_{60}Ge_6P_4^*C_{24}$
 $H_{60}N_2O_{18}P_4Ru_6^*C_{90}$
 $H_{60}N_6Zr_2^*C_{40}$
 $H_{60}NiO_{12}P_4^*C_{24}$
 $H_{60}O_{12}P_4Pt^*C_{24}$
 $H_{60}P_4Pd^*C_{24}$
 $H_{60}P_4Pt^*C_{72}$
 $H_{60}P_6Ru_2^*C_{21}$
 $H_{61}CoO_{12}P_4^*C_{72}$
 $H_{61}P_4Rh^*C_{72}$
 $H_{62}O_{12}P_4Ru^*C_{24}$
 $H_{62}Sn_6^*C_{72}$
 $H_{63}ClP_3Rh^*C_{63}$
 $H_{63}P_3Pd^*C_{27}$
 $H_{63}P_3Pt^*C_{27}$
 $H_{63}P_4Re^*C_{72}$
 $H_{64}BF_4O_4P_4Rh^*C_{62}$
 $H_{64}B_2Cu_2F_4P_4^*C_{72}$
 $H_{64}MoN_4P_4^*C_{60}$
 $H_{64}P_3Rh^*C_{26}$
 $H_{64}P_3Rh^*C_{27}$
 $H_{64}P_4W^*C_{76}$
 $H_{65}ClP_3Rh^*C_{63}$
 $H_{66}BF_4O_4P_4Rh^*C_{62}$
 $H_{66}BP_3Pd^*C_{42}$
 $H_{66}BrIrOP_2^*C_{37}$
 $H_{66}ClIrOP_2^*C_{37}$
 $H_{66}Cl_2NiP_2^*C_{36}$
 $H_{66}IiR_2OP_2^*C_{37}$
 $H_{66}NiP_2^*C_{36}$
 $H_{66}P_2Pt^*C_{36}$
 $H_{67}ClNiP_2^*C_{36}$
 $H_{67}F_5P_2Pt^*C_{42}$

$H_{68}MoP_4^*C_{60}$
 $H_{68}P_2Pt^*C_{36}$
 $H_{68}P_6Ru_3^*C_{75}$
 $H_{70}B_{10}Cu_2P_4^*C_{72}$
 $H_{71}NNiP_2^*C_{40}$
 $H_{72}Cl_3OsP_3^*C_{42}$
 $H_{72}Ge_2P_2Pt^*C_{54}$
 $H_{72}NiOP_2^*C_{42}$
 $H_{72}P_2Ru^*C_{36}$
 $H_{80}P_2Pt_2Si_2^*C_{40}$
 $H_{82}BIrP_4^*C_{64}$
 $H_{84}Cl_2Rh_2P_4^*C_{84}$
 $H_{84}P_4Pt_2^*C_{38}$
 $H_{84}P_4Pt_4^*C_{48}$
 $H_{85}CoO_{12}P_4^*C_{36}$
 $H_{87}P_3Pt_3^*C_{36}$
 $H_{88}P_4Ru_2^*C_{36}$
 $H_{90}Cl_4P_6Ru_2^*C_{60}$
 $H_{90}P_2Pt_2Si_2^*C_{52}$
 $H_{96}Al_2O_8P_8Ta_2^*C_{36}$
 Hf^*Co
 Hf^*H_2
 $HfNi$

Reaction with H_2 : 1.12.8.1.3

Structure: 1.12.8.1.3

HfV₂

Reaction with H_2 : 1.12.8.1.2

Hg

Reaction with HI and CF_3AsI_2 : 1.5.3.3.3

Reaction with HI and $(CF_3)_2AsI$:

1.5.3.3.3

Reduction and coupling of iodophosphines: 1.5.3.2.3

Reduction of CO_2 at electrode: 1.6.2.5

$Hg^*C_7H_3F_5$

Hg^*H

Hg^*H_2

$HgLi$

$LiHg$

Reaction with H_2 : 1.8.2.1

$HgNa$

$NaHg$

Reaction with H_2 : 1.8.2.2

$HgO_2^*C_8H_8$

$HgSn_2^*C_6H_{18}$

$HgSn_2^*C_{12}H_{30}$

$HgSn_2^*C_{18}H_{42}$

$HgSn_2^*C_{24}H_{54}$

Ho^*Co_2

Ho^*Fe_2

Ho^*H_2

HoNi₂Reaction with H₂: 1.12.8.1.2**HoRu₂**Reaction with H₂: 1.12.8.1.2**I*C₃AsF₆****I*C₂H₅****I*C₆H₅****I*Cu****I*GeH₃****I*Ge₂H₅****I*H****IrOP₂*C₁₉H₄₂****IrOP₂*C₃₇H₃₀****IrOP₂*C₃₇H₆₆****IrO₇P₂*C₃₇H₃₀****IMoN₂P₄*C₅₃H₅₁****IMoN₂P₄*C₅₃H₅₂BF₄****IN*C****IN*H₂****IN*H₄****INa****NaI**From CH₃ZnI and NaH: 1.9.4.1**IO₁₀Os₃*C₁₀H****IP*C₂F₆****IP*F₂****IP*H₄****IP₂Pt*C₁₂H₃₁****IW*C₁₁H₁₃****IZn*CH₃****I₂**Catalyst for reaction of H₂ with Mg:

1.8.3.2

I₂*Ba**I₂*CAsF₃****I₂*GeH₂****I₂Mg****MgI₂**Catalyst for reaction of H₂ with Mg:

1.8.3.2

I₂P*CF₃**I₂Sb*C₆H₅****I₂Th****ThI₂**

Formation of hydrides: 1.12.8.2.5

I₂Zn*AlH₃**I₃*GeH****I₃InLi*H****I₃P****PI₃**Deuterolysis with D₂O: 1.5.7.1.2

Hydrolysis: 1.5.3.2.1

I₄P₂**P₂I₄**Conversion to Ba[H₂P₂O₄]: 1.5.3.2.1

Hydrolysis in aq base: 1.5.3.2.1

Hydrolysis to form [H₂P₂O₄]²⁻ salts:

1.5.6.2

I₁₁Nb₆**Nb₆I₁₁**Reaction with H₂: 1.10.3.2**I₁₁Nb₆*H****In**Catalyst for reaction of H₂ with Mg:

1.8.3.2

In*Al₃H₁₂**In*B₃H₁₂****In*C₃H₉****In*Cl₃****In*H₃****InLi*AlCl₃H₄****InLi*BCl₃H₄****InLi*Br₃H****InLi*Cl₃H****InLi*HI₃****InLi*H₄****InP**

Reaction with aq acid: 1.5.3.2.1

Reaction with hydrogen: 1.5.2.2

Ir*C₁₄H₂₁**Ir*C₃₄H₃₈F₆P₃****IrH₂*Cl₆****IrNOP*C₂₉H₃₃B₁₀****IrNOP*C₂₉H₃₅B₁₀****IrNOP*C₃₄H₃₅B₁₀****IrNOP*C₃₄H₃₇B₁₀****IrNOP₂*C₃₆H₃₃Cl₃****IrNOP₃*C₅₄H₄₅****IrNO₂P*C₂₈H₂₁****IrNO₂P*C₂₈H₂₂Cl****IrNP₂*C₃₇H₃₁Cl****IrN₂P₂*C₄₀H₃₈BF₄****IrN₄O₉S₃*C₂₇H₁₆F₉****IrN₄P₃*C₄₂H₃₂F₁₂****IrNa₂*Cl₆****IrNa₂O₆*Cl₆H₁₂****IrO*C₃₇H₃₀As₂Cl****IrOP*C₁₉H₁₅Cl****IrOP₂*C₇H₁₈Cl****IrOP₂*C₁₃H₃₀Cl****IrOP₂*C₁₉H₄₂Br****IrOP₂*C₁₉H₄₂Cl****IrOP₂*C₁₉H₄₂I****IrOP₂*C₂₇H₂₄D₃**

$\text{IrOP}_2^*\text{C}_{27}\text{H}_{25}$	$\text{IrO}_5\text{P}_3^*\text{C}_{53}\text{H}_{42}\text{Fe}$
$\text{IrOP}_2^*\text{C}_{27}\text{H}_{27}$	$\text{IrO}_7\text{P}_2^*\text{C}_{37}\text{H}_{30}\text{Br}$
$\text{IrOP}_2^*\text{C}_{29}\text{H}_{37}\text{B}_{10}$	$\text{IrO}_7\text{P}_2^*\text{C}_{37}\text{H}_{30}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{29}\text{H}_{39}\text{B}_{10}$	$\text{IrO}_7\text{P}_2^*\text{C}_{37}\text{H}_{30}\text{I}$
$\text{IrOP}_2^*\text{C}_{30}\text{H}_{39}\text{B}_{10}$	$\text{IrO}_7\text{P}_2^*\text{C}_{39}\text{H}_{30}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{30}\text{H}_{41}\text{B}_{10}$	$\text{IrP}^*\text{C}_{13}\text{H}_{26}$
$\text{IrOP}_2^*\text{C}_{33}\text{H}_{38}\text{Cl}$	$\text{IrP}_2^*\text{C}_6\text{H}_{23}$
$\text{IrOP}_2^*\text{C}_{35}\text{H}_{39}\text{B}_{10}$	$\text{IrP}_2^*\text{C}_{21}\text{H}_{46}\text{Br}$
$\text{IrOP}_2^*\text{C}_{35}\text{H}_{41}\text{B}_{10}$	$\text{IrP}_2^*\text{C}_{21}\text{H}_{46}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{35}\text{H}_{43}\text{B}_{10}$	$\text{IrP}_2^*\text{C}_{21}\text{H}_{49}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{30}\text{Br}$	$\text{IrP}_2^*\text{C}_{22}\text{H}_{48}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{30}\text{Cl}$	$\text{IrP}_2^*\text{C}_{22}\text{H}_{51}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{30}\text{I}$	$\text{IrP}_2^*\text{C}_{26}\text{H}_{30}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{31}$	$\text{IrP}_2^*\text{C}_{36}\text{H}_{35}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{31}\text{Cl}_2$	$\text{IrP}_2^*\text{C}_{37}\text{H}_{30}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{31}\text{D}_2$	$\text{IrP}_2^*\text{C}_{44}\text{H}_{42}\text{BF}_4$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{32}\text{Cl}$	$\text{IrP}_2^*\text{C}_{44}\text{H}_{43}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{33}$	$\text{IrP}_2^*\text{C}_{45}\text{H}_{45}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{38}\text{B}_3$	$\text{IrP}_3^*\text{C}_9\text{H}_{28}\text{Cl}_4$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{66}\text{Br}$	$\text{IrP}_3^*\text{C}_{12}\text{H}_{51}\text{B}_{30}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{66}\text{Cl}$	$\text{IrP}_3^*\text{C}_{18}\text{H}_{45}\text{Cl}_3$
$\text{IrOP}_2^*\text{C}_{37}\text{H}_{66}\text{I}$	$\text{IrP}_3^*\text{C}_{18}\text{H}_{46}\text{Cl}_2$
$\text{IrOP}_2^*\text{C}_{39}\text{H}_{41}\text{B}_{10}$	$\text{IrP}_3^*\text{C}_{36}\text{H}_{37}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{39}\text{H}_{43}\text{B}_{10}$	$\text{IrP}_3^*\text{C}_{36}\text{H}_{39}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{40}\text{H}_{43}\text{B}_{10}$	$\text{IrP}_3^*\text{C}_{54}\text{H}_{45}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{40}\text{H}_{45}\text{B}_{10}$	$\text{IrP}_3^*\text{C}_{54}\text{H}_{48}$
$\text{IrOP}_2^*\text{C}_{43}\text{H}_{42}\text{Cl}$	$\text{IrP}_4^*\text{C}_{54}\text{H}_{48}\text{Cl}$
$\text{IrOP}_2^*\text{C}_{45}\text{H}_{45}\text{B}_{10}$	$\text{IrP}_4^*\text{C}_{64}\text{H}_{82}\text{B}$
$\text{IrOP}_2^*\text{C}_{45}\text{H}_{47}\text{B}_{10}$	$\text{IrP}_5^*\text{C}_{12}\text{H}_{36}\text{F}_6$
$\text{IrOP}_3^*\text{C}_{39}\text{H}_{41}\text{B}_{10}$	$\text{IrS}^*\text{C}_{36}\text{H}_{32}\text{ClP}_2$
$\text{IrOP}_3^*\text{C}_{55}\text{H}_{46}$	$\text{IrSi}^*\text{C}_{16}\text{H}_{32}\text{Cl}$
$\text{IrOP}_4^*\text{C}_{13}\text{H}_{32}\text{Cl}$	$\text{Ir}_2^*\text{C}_{16}\text{H}_{24}\text{Cl}_2$
$\text{IrOP}_5^*\text{C}_{13}\text{H}_{38}\text{F}_6$	$\text{Ir}_2^*\text{C}_{16}\text{H}_{26}\text{Cl}_4$
$\text{IrO}_2^*\text{C}_{12}\text{H}_{15}$	$\text{Ir}_2^*\text{C}_{20}\text{H}_{17}\text{Cl}_2$
$\text{IrO}_2^*\text{C}_{12}\text{H}_{16}\text{BF}_4$	$\text{Ir}_2^*\text{C}_{32}\text{H}_{56}\text{Cl}_2$
$\text{IrO}_2^*\text{C}_{16}\text{H}_{15}$	$\text{Ir}_2\text{N}_6\text{O}_2\text{P}_2\text{S}_2^*\text{C}_{16}\text{H}_{36}$
$\text{IrO}_2\text{P}^*\text{C}_{28}\text{H}_{32}\text{B}_{10}$	$\text{Ir}_2\text{N}_6\text{O}_2\text{P}_3\text{S}_2^*\text{C}_{16}\text{H}_{38}$
$\text{IrO}_2\text{P}_2^*\text{C}_{36}\text{H}_{36}\text{BF}_4$	$\text{Ir}_2\text{O}_2\text{P}_2\text{S}_2^*\text{C}_{16}\text{H}_{36}$
$\text{IrO}_2\text{P}_2^*\text{C}_{38}\text{H}_{31}$	$\text{Ir}_2\text{O}_2\text{P}_2\text{S}_2^*\text{C}_{16}\text{H}_{38}$
$\text{IrO}_2\text{P}_2^*\text{C}_{38}\text{H}_{40}\text{BF}_4$	$\text{Ir}_2\text{O}_2\text{P}_2\text{S}_2^*\text{C}_{46}\text{H}_{48}$
$\text{IrO}_2\text{P}_2^*\text{C}_{40}\text{H}_{44}\text{BF}_4$	$\text{Ir}_2\text{O}_2\text{P}_2\text{S}_2^*\text{C}_{46}\text{H}_{50}$
$\text{IrO}_2\text{P}_2^*\text{C}_{42}\text{H}_{44}\text{BF}_4$	$\text{Ir}_2\text{O}_8\text{P}_2\text{S}_2^*\text{C}_{16}\text{H}_{36}$
$\text{IrO}_2\text{P}_2^*\text{C}_{42}\text{H}_{48}\text{BF}_4$	$\text{Ir}_2\text{O}_8\text{P}_2\text{S}_2^*\text{C}_{16}\text{H}_{38}$
$\text{IrO}_2\text{P}_2^*\text{C}_{44}\text{H}_{48}\text{BF}_4$	$\text{Ir}_4\text{O}_{12}^*\text{C}_{12}$
$\text{IrO}_2\text{P}_2^*\text{C}_{44}\text{H}_{52}\text{BF}_4$	K^*AlH_4
$\text{IrO}_3\text{P}^*\text{C}_{29}\text{H}_{30}\text{B}_{10}$	K^*AsH_2
$\text{IrO}_3\text{P}^*\text{C}_{29}\text{H}_{32}\text{B}_{10}$	K^*BGeH_6
$\text{IrO}_3\text{P}_3^*\text{C}_{39}\text{H}_{30}\text{F}_6$	K^*BH_4
$\text{IrO}_4\text{P}_2^*\text{C}_{40}\text{H}_{33}$	$\text{K}^*\text{B}_4\text{H}_9$
$\text{IrO}_4\text{P}_3^*\text{C}_{52}\text{H}_{40}\text{Fe}$	$\text{K}^*\text{B}_5\text{H}_{12}$
$\text{IrO}_4\text{P}_3^*\text{C}_{52}\text{H}_{44}\text{Fe}$	$\text{K}^*\text{B}_6\text{H}_9$
$\text{IrO}_5\text{P}_3^*\text{C}_{53}\text{H}_{40}\text{Fe}$	$\text{K}^*\text{B}_6\text{H}_{11}$

K*B₇H₁₂
K*B₉D₃H₁₁
K*B₉D₃H₉
K*B₉H₁₄
K*C₃H₁₀B
K*C₃H₁₂BGe
K*C₆H₁₅Ge
K*C₁₂H₂₈B
K*C₁₈H₁₅Ge
K*C₁₈H₁₆B
K*C₂₁H₂₁Ge
K*C_uH₂
K*F₂H
K*GeH₃
K*H
KN*C
KN*H₂
KO*CH
KO₂*CH
KO₂Ru*C₁₂H₁₅
KO₂Sn*CH₃
KO₃*C₉H₂₂B
KO₄*C₄HFe
KO₁₀*C₁₀HCr₂
KO₁₃Ru₃*C₁₃Co
KO₁₃Ru₄*C₁₃H
KO₁₅*C₁₅HCo₆
KP*CHF₇
KP*C₂HF₉
KP*F₅H
KP*H₂
KP₃*C₈H₁₈
KP₄Rh*F₁₂
KSi*AsH₄
KSi*H₃
KZn*C₂H₇
KZn₂*C₄H₁₃
KZn₂*H₅
K₂*C₂
K₂N*C₄H₁₀As
K₂N*H
K₂O₁₃Ru₄*C₁₃
K₂O₁₅*C₁₅Co₆
K₂P₂*C₈H₁₈
K₂P₄*C₄H₁₂
K₂P₄*C₈H₂₀
K₂P₄*C₂₄H₄₄
K₂Zn*H₄
K₂Zn₃*B₈H₃₂
K₃*As
K₃N

Reaction with protonic acids: 1.5.3.1.3

K₃Sb

Hydrolysis: 1.5.3.4

K₄N₂O₆P₂

K₄[O₃PNNPO₃]

Hydrolysis to N₂H₄: 1.5.3.1.1

K₄N₇W*C₇H

K₄O₁₂Ru₄*C₁₂

K₅N₇W*C₇

La*Co₅

La*Cu₅

La*H₂

LaMg₂

Reaction with H₂: 1.12.8.1.2

LaNi₂

Reaction with H₂: 1.12.8.1.2

LaNi₅

Catalyst for reaction of H₂ with Mg:

1.8.3.2

Catalyst in formation of NbH₂: 1.12.6

Hydrides: 1.12.8.1.3

Reaction with H₂: 1.12.8.1.1

LaNi₅*H₆

LaPt₅

Reaction with H₂: 1.12.8.1.1

LaRh₂

Reaction with H₂: 1.12.8.1.2

LaRu₂

Reaction with H₂: 1.12.8.1.2

La₂O₃-Pd

Pd-La₂O₃

Catalysis of CO-H₂ reaction: 1.6.2.1.2

Li

Reaction with H₂: 1.8.2.1

Reduction of C₆H₅CH=CH₂ in liq

NH₃: 1.6.3.1.2

Li*AlAs₄H₈

Li*AlCl₃H₄In

Li*AlCl₄

Li*AlD₄

Li*AlH₄

Li*AlH₄

Li*AlH₄

Li*BCl₃H₄In

Li*BD₄

Li*BF₄

Li*BH₄

Li*B₂H₇

Li*Br₃HIIn

Li*CH₃

Li*C₂H₅

Li*C₃H₇

Li*C₄H₉

$\text{Li}^*\text{C}_4\text{H}_{12}\text{Al}$
 $\text{Li}^*\text{C}_5\text{H}_5$
 $\text{Li}^*\text{C}_6\text{H}_{15}\text{BD}$
 $\text{Li}^*\text{C}_6\text{H}_{15}\text{Ge}$
 $\text{Li}^*\text{C}_6\text{H}_{16}\text{B}$
 $\text{Li}^*\text{C}_6\text{H}_{19}\text{B}_2$
 $\text{Li}^*\text{C}_6\text{H}_9\text{AlCl}$
 $\text{Li}^*\text{C}_{18}\text{H}_{15}\text{Ge}$
 $\text{Li}^*\text{C}_{21}\text{H}_{21}\text{Ge}$
 $\text{Li}^*\text{C}_{54}\text{H}_{45}\text{Ge}_4$
 $\text{Li}^*\text{Cl}_3\text{HIn}$
 Li^*CuH_2
 $\text{Li}^*\text{Cu}_2\text{H}_3$
 Li^*D
 Li^*GaH_4
 Li^*GeH_3
 Li^*H
 $\text{Li}^*\text{HI}_3\text{In}$
 $\text{Li}^*\text{H}_4\text{In}$
 Li^*Hg
 LiN^*H_2
 $\text{LiO}^*\text{CH}_4\text{Al}$
 $\text{LiOSi}^*\text{C}_{31}\text{H}_{25}$
 LiO_2^*CH
 $\text{LiO}_2\text{P}^*\text{C}_{18}\text{H}_{20}$
 $\text{LiO}_3^*\text{C}_3\text{H}_{10}\text{B}$
 $\text{LiO}_3^*\text{C}_{12}\text{H}_{28}\text{Al}$
 $\text{LiO}_4^*\text{C}_2\text{H}_4\text{Al}$
 $\text{LiO}_4^*\text{C}_2\text{H}_4\text{B}$
 $\text{LiO}_4^*\text{C}_4\text{H}_{12}\text{Al}$
 $\text{LiO}_5^*\text{C}_4\text{H}_{10}\text{B}$
 $\text{LiO}_8^*\text{C}_4\text{H}_4\text{Al}$
 $\text{LiP}^*\text{C}_4\text{H}_{10}$
 $\text{LiP}^*\text{C}_{12}\text{H}_{10}$
 LiP^*H_2
 LiPSi^*H_4
 $\text{LiPSi}_2^*\text{H}_6$
 LiP_5^*H_4
 $\text{LiPb}^*\text{C}_6\text{H}_{15}$
 $\text{LiPb}^*\text{C}_{18}\text{H}_{15}$
 $\text{LiPb}^*\text{C}_{18}\text{H}_{33}$
 $\text{LiSb}^*\text{C}_2\text{H}_6$
 $\text{LiSb}^*\text{C}_4\text{H}_{10}$
 $\text{LiSb}^*\text{C}_{12}\text{H}_{10}$
 $\text{LiSi}^*\text{C}_{18}\text{H}_{18}\text{Al}$
 LiSi^*H_3
 $\text{LiSn}^*\text{C}_{12}\text{H}_{27}$
 $\text{LiSn}^*\text{C}_{18}\text{H}_{15}$
 LiTi^*H_4
 $\text{LiZn}^*\text{C}_2\text{H}_{10}\text{Al}$
 LiZn^*H_3
 $\text{LiZn}_2^*\text{C}_4\text{H}_{16}\text{Al}$

$\text{Li}_2^*\text{B}_4\text{CdH}_{16}$
 Li_2^*C_2
 $\text{Li}_2^*\text{C}_2\text{H}_{14}\text{B}_{10}$
 $\text{Li}_2^*\text{CuH}_3$
 $\text{Li}_2^*\text{Cu}_3\text{H}_5$
 $\text{Li}_2\text{N}^*\text{H}$
 $\text{Li}_2\text{P}_4^*\text{C}_4\text{H}_{12}$
 $\text{Li}_2\text{P}_4^*\text{C}_8\text{H}_{20}$
 $\text{Li}_2\text{P}_4^*\text{C}_{24}\text{H}_{44}$
 $\text{Li}_2\text{P}_7^*\text{H}$
 $\text{Li}_2\text{Si}_2^*\text{C}_4\text{H}_{12}$
 $\text{Li}_2\text{Si}_3^*\text{C}_6\text{H}_{18}$
 $\text{Li}_2\text{Si}_4^*\text{C}_8\text{H}_{24}$
 $\text{Li}_2\text{Si}_5^*\text{C}_{10}\text{H}_{30}$
 $\text{Li}_2\text{Si}_6^*\text{C}_{12}\text{H}_{36}$
 $\text{Li}_2\text{Zn}^*\text{B}_4\text{H}_{16}$
 $\text{Li}_2\text{Zn}^*\text{H}_4$
 $\text{Li}_3^*\text{CuH}_4$
 Li_3N

Reaction with protonic acids: 1.5.3.1.3

$\text{Li}_3\text{Zn}^*\text{H}_5$

$\text{Li}_4^*\text{CuH}_5$

Li_6Si_2

Hydrolysis: 1.6.3.2.1

Lu^*Fe_2

Lu^*H_2

Mg

Reaction with Sn in H_2SO_4 : 1.6.3.4.1

Reaction with $\text{C}_6\text{H}_5\text{CHO}$ to form

MgH_2 : 1.8.3.2

Reaction with H_2 : 1.8.3, 1.8.3.2

Reduction of Ge(IV) species in H_2O :

1.6.3.3.1

Reduction of P_4 in H_2O to form PH_3 :

1.5.6.2

Use in industrial reduction of nitro compounds: 1.5.6.1

Mg^*B_2

Mg^*Br_2

$\text{Mg}^*\text{C}_2\text{H}_5\text{Br}$

$\text{Mg}^*\text{C}_2\text{H}_5\text{Cl}$

$\text{Mg}^*\text{C}_2\text{H}_6$

$\text{Mg}^*\text{C}_3\text{H}_7\text{Cl}$

$\text{Mg}^*\text{C}_4\text{H}_9\text{Br}$

$\text{Mg}^*\text{C}_4\text{H}_{10}$

$\text{Mg}^*\text{C}_6\text{H}_{11}\text{Br}$

$\text{Mg}^*\text{C}_6\text{H}_{11}\text{Cl}$

$\text{Mg}^*\text{C}_6\text{H}_{15}\text{ClGe}$

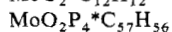
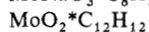
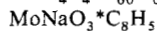
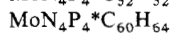
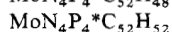
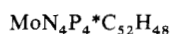
$\text{Mg}^*\text{C}_9\text{H}_{21}\text{ClGe}$

$\text{Mg}^*\text{C}_{14}\text{H}_{10}$

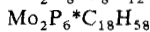
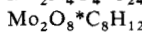
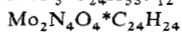
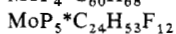
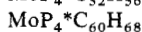
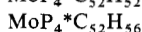
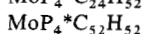
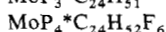
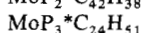
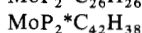
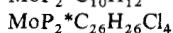
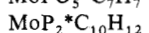
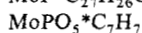
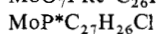
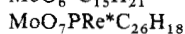
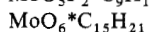
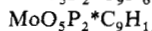
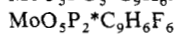
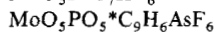
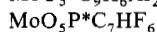
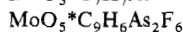
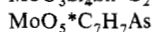
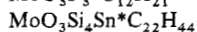
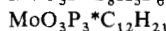
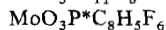
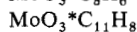
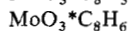
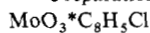
$\text{Mg}^*\text{C}_{18}\text{H}_{15}\text{ClGe}$

$\text{Mg}^*\text{C}_{18}\text{H}_{33}\text{ClGe}$

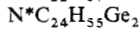
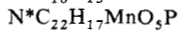
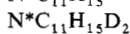
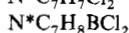
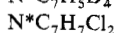
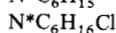
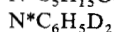
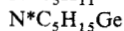
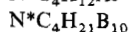
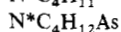
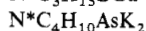
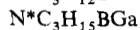
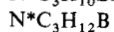
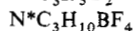
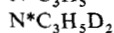
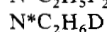
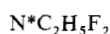
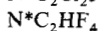
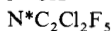
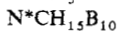
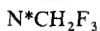
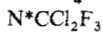
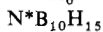
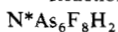
- Mg*H₂**
Mg*I₂
MgN₂*H₄
MgN₂Ti*C₁₀H₁₀Cl
MgN₂Ti₂*C₂₀H₂₀Cl
MgSi*C₁₈H₁₅Br
MgSn₂*C₃₆H₃₀
MgZn*H₄
Mg₂*C₃
Mg₂*Ce
Mg₂*Cu
Mg₂*Ge
Mg₂*La
Mg₂NO₅Ti*C₁₃H₂₄Cl₂
Mg₂NO₅V*C₁₃H₂₄Cl₂
Mg₂Nd
 NdMg₂
 Reaction with H₂: 1.12.8.1.2
Mg₂Ni
 Reaction with H₂: 1.12.8.1.3
Mg₂Pb
 Reaction with aq acid: 1.6.3.5
Mg₂Si
 Deuterolysis with D₂O: 1.6.7.1.2
 Hydrolysis in aq acid: 1.6.3.2.1
 Protonation by H₂SO₄: 1.6.6.2
 Protonation in liq NH₃: 1.6.3.2.2
Mg₂Sm
 SmMg₂
 Reaction with H₂: 1.12.8.1.2
Mg₂Sn
 Deuterolysis with D₂O: 1.6.7.1.4
 Protonation by NH₄Br: 1.6.3.4.2
 Reactions with protonic acids: 1.6.3.4.1
Mg₂Y
 YMg₂
 Reaction with H₂: 1.12.8.1.2
Mg₃*As₂
Mg₃*B₂
Mg₃*Bi₂
Mg₃N₂
 Deuterolysis with D₂O: 1.5.6.1, 1.5.7.1.1
 Hydrolysis to NH₃: 1.5.3.1.1
Mg₃P₂
 Reaction with aq acid: 1.5.3.2.1
Mg₃Sb₂
 Reaction with aq HCl: 1.5.3.4
Mg₄Si*Ge
Mg₂₀Si₉*Ge
Mn
 Oxidative addition of CH₄: 1.10.5.3
Mn*H
- MnNO₁₂Os₂*C₁₆H₁₂**
MnOP*C₂₅H₂₂
MnOP*C₂₅H₂₃
MnO₂P*C₁₅H₁₆
MnO₂Si*C₂₀H₁₈Cl
MnO₂Si*C₂₅H₂₃
MnO₃*C₉H₇
MnO₄P*C₂₂H₁₆
MnO₅*C₅H
MnO₅PN*C₂₂H₁₇
MnO₅P₂*C₂₃H₁₅Au
MnO₅P₂*C₂₃H₁₅F₆
MnO₆*C₆BF₄
MnO₈*C₆F₃
MnO₁₂Os₂*C₁₂H
Mn₂*Dy
Mn₂*Er
Mn₂*Gd
Mn₂O₄P₂*C₂₆H₂₂
Mn₂O₁₀*C₁₀
Mn₂Se
 SeMn₂
 Reaction with H₂: 1.12.8.1.2
Mn₂Sm
 SmMn₂
 Reaction with H₂: 1.12.8.1.2
Mn₂Y
 YMn₂
 Reaction with H₂: 1.12.8.1.2
Mn₂Zr
 ZrMn₂
 Reaction with H₂: 1.12.8.1.2
Mo*C₁₀H₁₂
Mo*C₁₈H₁₆
Mo*C₃₃H₂₅Cl
Mo*C₃₃H₂₆
Mo*D₂
Mo*H
MoNO₄P*C₆H₉
MoNP₄*C₅₂H₄₉Br₂
MoN₂O₄P₄S*C₅₂H₅₁
MoN₂P₃*C₂₄H₃₅Br₂
MoN₂P₄*C₅₂H₅₀Br₂
MoN₂P₄*C₅₃H₅₁I
MoN₂P₄*C₅₃H₅₂BF₄I
MoN₂P₄*C₅₆H₅₇Br
MoN₂P₄*C₅₇H₅₈
MoN₃O₃*C₆H₁₆BF₄
MoN₃O₆*C₆H₁₃Cl
MoN₄*C₈H₂₄
MoN₄P₃*C₂₈H₂₈
MoN₄P₄*C₃₂H₄₄



Preparation of hydride: 1.12.8.2.3



Reaction with alkanes: 1.5.4.1.2



- $\text{N}^*\text{H}_2\text{K}$
 $\text{N}^*\text{H}_2\text{Li}$
 N^*H_3
 $\text{N}^*\text{H}_4\text{I}$
 N^*K_3
 N^*Li_3
 $\text{NNa}^*\text{CH}_3\text{B}$
 $\text{NNa}^*\text{C}_2\text{H}_6$
 NNa^*H_3
 NNaO^*C
 $\text{NNaSi}_2^*\text{C}_6\text{H}_{18}$
 NNa_2^*H
 NNa_3
 Na_3N
 Reaction with protonic acids: 1.5.3.1.3
 $\text{NNiP}_2^*\text{C}_{40}\text{H}_{71}$
NO
 Reaction with H_2 : 1.5.2.1.2
 NO^*CH
 $\text{NO}^*\text{C}_6\text{H}_5$
 $\text{NO}^*\text{C}_7\text{H}_5$
 $\text{NO}^*\text{C}_7\text{H}_7$
 $\text{NO}^*\text{C}_8\text{H}_9$
 $\text{NO}^*\text{C}_{11}\text{H}_{15}$
 NO^*H_3
 $\text{NOP}^*\text{C}_8\text{H}_{10}$
 $\text{NOP}^*\text{C}_{11}\text{H}_{16}$
 $\text{NOP}^*\text{C}_{14}\text{H}_{16}$
 $\text{NOP}^*\text{C}_{29}\text{H}_{33}\text{B}_{10}\text{Ir}$
 $\text{NOP}^*\text{C}_{29}\text{H}_{35}\text{B}_{10}\text{Ir}$
 $\text{NOP}^*\text{C}_{34}\text{H}_{35}\text{B}_{10}\text{Ir}$
 $\text{NOP}^*\text{C}_{34}\text{H}_{37}\text{B}_{10}\text{Ir}$
 $\text{NOPPt}^*\text{C}_{27}\text{H}_{26}\text{Cl}_2$
 $\text{NOPRe}^*\text{C}_{23}\text{H}_{21}$
 $\text{NOPS}^*\text{C}_{14}\text{H}_{16}$
 $\text{NOP}_2^*\text{C}_{36}\text{H}_{33}\text{Cl}_3\text{Ir}$
 $\text{NOP}_2^*\text{Cl}_5$
 $\text{NOP}_2\text{Pt}^*\text{C}_{19}\text{H}_{36}\text{Cl}$
 $\text{NOP}_2\text{Pt}^*\text{C}_{43}\text{H}_{36}\text{Cl}$
 $\text{NOP}_3^*\text{C}_{54}\text{H}_{45}\text{Ir}$
 $\text{NOP}_3\text{Ru}^*\text{C}_{54}\text{H}_{46}$
 NORu^*Cl_3
 $\text{NOSn}^*\text{C}_{13}\text{H}_{21}$
 $\text{NO}_2^*\text{C}_2\text{H}_5$
 $\text{NO}_2^*\text{C}_3\text{H}_5$
 $\text{NO}_2^*\text{C}_4\text{H}_4\text{Br}$
 $\text{NO}_2^*\text{C}_4\text{H}_5$
 $\text{NO}_2^*\text{C}_4\text{H}_9$
 $\text{NO}_2^*\text{C}_6\text{H}_5$
 $\text{NO}_2^*\text{C}_6\text{H}_{11}$
 $\text{NO}_2^*\text{C}_6\text{H}_{15}$
 $\text{NO}_2^*\text{C}_{10}\text{H}_9\text{Fe}$
 $\text{NO}_2^*\text{C}_{10}\text{H}_{10}\text{Fe}$
 NO_2^*H
 $\text{NO}_2\text{OsP}_2^*\text{C}_{37}\text{H}_{30}\text{Cl}$
 $\text{NO}_2\text{OsP}_2^*\text{C}_{37}\text{H}_{31}\text{Cl}_2$
 $\text{NO}_2\text{P}^*\text{C}_{10}\text{H}_{14}$
 $\text{NO}_2\text{P}^*\text{C}_{10}\text{H}_{16}$
 $\text{NO}_2\text{P}^*\text{C}_{14}\text{H}_{16}$
 $\text{NO}_2\text{P}^*\text{C}_{28}\text{H}_{21}\text{Ir}$
 $\text{NO}_2\text{P}^*\text{C}_{28}\text{H}_{22}\text{ClIr}$
 $\text{NO}_2\text{P}_2\text{V}^*\text{C}_{43}\text{H}_{39}\text{B}$
 $\text{NO}_2\text{Re}^*\text{C}_6\text{H}_6$
 $\text{NO}_2\text{Re}^*\text{C}_7\text{H}_8$
 $\text{NO}_3^*\text{C}_7\text{H}_4\text{Cl}$
 $\text{NO}_3^*\text{C}_7\text{H}_5$
 $\text{NO}_3\text{P}^*\text{C}_6\text{H}_{12}$
 $\text{NO}_3\text{P}^*\text{C}_6\text{H}_{13}\text{BF}_4$
 $\text{NO}_3\text{P}^*\text{C}_8\text{H}_{10}$
 $\text{NO}_3\text{P}^*\text{C}_{10}\text{H}_{14}$
 $\text{NO}_3\text{P}^*\text{C}_{11}\text{H}_{14}$
 $\text{NO}_3\text{P}^*\text{C}_{12}\text{H}_{16}$
 $\text{NO}_3\text{P}^*\text{C}_{12}\text{H}_{18}$
 $\text{NO}_3\text{PRe}^*\text{C}_7\text{H}_5\text{F}_6$
 $\text{NO}_3\text{PRe}^*\text{C}_{24}\text{H}_{21}$
 $\text{NO}_3\text{Re}^*\text{C}_7\text{H}_6$
 $\text{NO}_3\text{Re}^*\text{C}_7\text{H}_8$
 $\text{NO}_3\text{S}^*\text{H}_3$
 $\text{NO}_3\text{V}^*\text{C}_{44}\text{H}_{36}$
 $\text{NO}_4^*\text{C}_{14}\text{H}_{15}$
 $\text{NO}_4^*\text{C}_{14}\text{H}_{17}$
 $\text{NO}_4\text{P}^*\text{C}_6\text{H}_9\text{Mo}$
 $\text{NO}_4\text{PS}^*\text{C}_{12}\text{H}_8\text{Cl}_2$
 $\text{NO}_4\text{P}_2^*\text{C}_{40}\text{H}_{31}\text{Fe}$
 $\text{NO}_4\text{Re}^*\text{C}_7\text{H}_6$
 $\text{NO}_4\text{S}^*\text{H}_3$
 $\text{NO}_5^*\text{C}_{14}\text{H}_{15}$
 $\text{NO}_5^*\text{C}_{14}\text{H}_{17}$
 $\text{NO}_5\text{Ti}^*\text{C}_{13}\text{H}_{24}\text{Cl}_2\text{Mg}_2$
 $\text{NO}_5\text{V}^*\text{C}_{13}\text{H}_{24}\text{Cl}_2\text{Mg}_2$
 $\text{NO}_6\text{PS}^*\text{C}_{18}\text{H}_{13}\text{Cl}$
 $\text{NO}_6\text{P}_2^*\text{C}_4\text{H}_{13}$
 $\text{NO}_6\text{P}_2^*\text{C}_8\text{H}_{21}$
 $\text{NO}_6\text{P}_2^*\text{C}_{12}\text{H}_{29}$
 $\text{NO}_6\text{S}_2^*\text{H}_3$
 $\text{NO}_8\text{Os}_3^*\text{C}_{10}\text{H}_6\text{F}_3$
 $\text{NO}_8\text{P}_2^*\text{C}_{44}\text{H}_{31}\text{Fe}_2$
 $\text{NO}_9\text{Os}_3^*\text{C}_{11}\text{H}_4\text{F}_3$
 $\text{NO}_9\text{Os}_3^*\text{C}_{15}\text{H}_7$
 $\text{NO}_9\text{Os}_3^*\text{C}_{17}\text{H}_{12}$
 $\text{NO}_9\text{Re}_2^*\text{C}_{17}\text{H}_{21}$
 $\text{NO}_9\text{Ru}_3^*\text{C}_{14}\text{H}_{11}$
 $\text{NO}_{10}^*\text{C}_{18}\text{H}_{21}\text{Cr}_2$
 $\text{NO}_{10}\text{Os}_3^*\text{C}_{12}\text{H}_2\text{F}_3$

$\text{NO}_{10}\text{Os}_3*\text{C}_{12}\text{H}_4\text{F}_3$
 $\text{NO}_{10}\text{Os}_3*\text{C}_{16}\text{H}_7$
 $\text{NO}_{10}\text{Ru}_3*\text{C}_{15}\text{H}_9$
 $\text{NO}_{11}*\text{C}_{15}\text{H}_{13}\text{Fe}_3$
 $\text{NO}_{11}\text{Os}_3*\text{C}_{13}\text{H}_3$
 $\text{NO}_{11}\text{Os}_3*\text{C}_{29}\text{H}_{16}$
 $\text{NO}_{11}\text{Ru}_3*\text{C}_{10}\text{H}$
 $\text{NO}_{11}\text{Ru}_3*\text{C}_{16}\text{H}_9$
 $\text{NO}_{11}\text{Ru}_3*\text{C}_{27}\text{H}_{37}$
 $\text{NO}_{11}\text{Ru}_4*\text{C}_{16}\text{H}_{13}$
 $\text{NO}_{12}*\text{C}_{12}\text{HFe}_4$
 $\text{NO}_{12}\text{Os}_2*\text{C}_{16}\text{H}_{12}\text{Mn}$
 $\text{NO}_{12}\text{P}*\text{C}_{22}\text{H}_{27}\text{Co}_3\text{Fe}$
 $\text{NO}_{13}*\text{C}_{18}\text{H}_7\text{Fe}_4$
 $\text{NO}_{14}*\text{C}_{14}\text{HFe}_5$
 $\text{NO}_{18}\text{P}_2\text{Ru}_6*\text{C}_{54}\text{H}_{31}$
 $\text{NP}*\text{C}_2\text{HCl}_7$
 $\text{NP}*\text{C}_2\text{H}_2\text{Cl}_7\text{F}$
 $\text{NP}*\text{C}_2\text{H}_6\text{F}_2$
 $\text{NP}*\text{C}_2\text{H}_3\text{F}_5$
 $\text{NP}*\text{C}_3\text{H}_6$
 $\text{NP}*\text{C}_4\text{H}_{12}$
 $\text{NP}*\text{C}_6\text{H}_8$
 $\text{NP}*\text{C}_6\text{H}_{16}$
 $\text{NP}*\text{C}_8\text{H}_{20}$
 $\text{NP}*\text{C}_{11}\text{H}_{17}$
 $\text{NP}*\text{C}_{12}\text{H}_{28}$
 $\text{NP}*\text{C}_{16}\text{H}_{20}$
 $\text{NP}*\text{C}_{17}\text{H}_{20}$
 $\text{NP}*\text{C}_{18}\text{H}_{15}\text{Br}$
 $\text{NP}*\text{C}_{18}\text{H}_{16}$
 $\text{NP}*\text{C}_{18}\text{H}_{17}\text{Br}$
 $\text{NP}*\text{C}_{18}\text{H}_{17}\text{Cl}$
 $\text{NP}*\text{C}_{19}\text{H}_{18}$
 $\text{NP}*\text{C}_{20}\text{H}_{20}$
 $\text{NP}*\text{C}_{24}\text{H}_{20}$
 $\text{NP}*\text{F}_2\text{H}_2$
 $\text{NPPt}*\text{C}_{25}\text{H}_{20}\text{Cl}_2$
 $\text{NPSSi}*\text{C}_5\text{H}_{16}$
 $\text{NPSSi}*\text{C}_{11}\text{H}_{27}$
 $\text{NPSSi}_2*\text{C}_8\text{H}_{24}$
 $\text{NPS}_3*\text{C}_2\text{H}_9$
 $\text{NPSi}*\text{C}_{26}\text{H}_{33}$
 $\text{NPSi}_2*\text{C}_6\text{H}_{18}\text{F}_2$
 $\text{NPSi}_2*\text{C}_6\text{H}_{20}$
 $\text{NPSi}_3*\text{C}_9\text{H}_{27}$
 $\text{NP}_2*\text{C}_{37}\text{H}_{31}\text{ClIr}$
 $\text{NP}_2\text{Pt}*\text{C}_{18}\text{H}_{36}\text{Cl}$
 $\text{NP}_2\text{Pt}*\text{C}_{37}\text{H}_{31}$
 $\text{NP}_2\text{Pt}*\text{C}_{39}\text{H}_{31}\text{F}_6$
 $\text{NP}_2\text{Pt}*\text{C}_{42}\text{H}_{36}\text{Cl}$
 $\text{NP}_2\text{Re}*\text{C}_{12}\text{H}_{23}\text{Cl}_3$

$\text{NP}_2\text{Re}*\text{C}_{12}\text{H}_{30}$
 $\text{NP}_2\text{Re}*\text{C}_{43}\text{H}_{37}\text{Cl}_3$
 $\text{NP}_2\text{Re}*\text{C}_{43}\text{H}_{38}\text{Cl}_2$
 $\text{NP}_2\text{Rh}*\text{C}_{47}\text{H}_{47}\text{Cl}$
 $\text{NP}_2\text{Rh}*\text{C}_{47}\text{H}_{49}\text{Cl}$
 $\text{NP}_3*\text{C}_{31}\text{H}_{32}$
 $\text{NP}_3*\text{C}_{55}\text{H}_{48}\text{BCu}$
 $\text{NP}_4*\text{C}_{52}\text{H}_{49}\text{Br}_2\text{Mo}$
 $\text{NPb}*\text{C}_7\text{H}_{19}$
 $\text{NRb}*\text{H}_2$
 $\text{NS}*\text{C}_3\text{H}_5$
 $\text{NSSi}*\text{C}_9\text{H}_{21}$
 $\text{NSb}*\text{C}_6\text{H}_9\text{Cl}_5$
 $\text{NSi}*\text{C}_3\text{H}_9\text{D}_2$
 $\text{NSi}*\text{C}_4\text{H}_{12}\text{Cl}$
 $\text{NSi}*\text{C}_6\text{H}_{17}$
 $\text{NSi}*\text{C}_7\text{H}_{19}$
 $\text{NSi}_2*\text{C}_6\text{H}_{19}$
 $\text{NSi}_2*\text{C}_7\text{H}_{31}\text{B}_{10}$
 $\text{NSi}_2*\text{C}_{12}\text{H}_{23}$
 NSi_3*H_9
 $\text{NSn}*\text{C}_5\text{H}_{15}$
 $\text{NSn}*\text{C}_6\text{H}_9\text{F}_6$
 $\text{NSn}*\text{C}_7\text{H}_{19}$
 $\text{NSn}*\text{C}_8\text{H}_{21}$
 $\text{NSn}*\text{C}_{10}\text{H}_{25}$
 $\text{NSn}*\text{C}_{14}\text{H}_{33}$
 $\text{NSn}*\text{C}_{22}\text{H}_{25}$
 $\text{NSn}*\text{C}_{25}\text{H}_{39}$
 $\text{NSn}*\text{C}_{42}\text{H}_{45}\text{Ge}_2$
 $\text{NYb}*\text{C}_{10}\text{H}_{12}$
 $\text{NYb}*\text{C}_{15}\text{H}_{18}$

N₂

Electrolytic reduction to NH_3 : 1.5.3.1.1
 Impurity in H_2 : 1.8.2
 Reaction with D_2 : 1.5.7.1.1
 Reaction with CsH : 1.5.4.1.1
 Reaction with RbH : 1.5.4.1.1
 Reaction with H_2 : 1.5.2.1.1, 1.5.6.1
 Reduction by $\text{V}(\text{OH})_2$: 1.5.3.1.1
 Reduction to NH_3 : 1.5.5.1
 Reduction with aq $\text{Na}[\text{BH}_4]$, sulfur donor ligands and Mo and Fe salts: 1.5.5.1

N_2*BaH_4
 N_2*Ba_3
 N_2*Be_3
 N_2*CCa
 N_2*CH_2
 $\text{N}_2*\text{C}_2\text{Ca}$
 $\text{N}_2*\text{C}_2\text{H}_8$
 $\text{N}_2*\text{C}_3\text{H}_6$

$N_2 * C_4 H_{13} B$
 $N_2 * C_5 H_{14}$
 $N_2 * C_6 H_{16}$
 $N_2 * C_{10} H_{24}$
 $N_2 * C_{13} H_{10}$
 $N_2 * C_{13} H_{22}$
 $N_2 * C_{16} H_{53} B_{10} Cl_2 Cu$
 $N_2 * CaH_4$
 $N_2 * Ca_3$
 $N_2 * CdH_4$
 $N_2 * F_4$
 $N_2 * Ge_3$
 $N_2 * H_4$
 $N_2 * H_4 Mg$
 $N_2 * Mg_3$
 $N_2 O$

Reduction to NH_3 : 1.5.5.1

$N_2 O * CH_4$
 $N_2 O * C_{14} H_{14}$
 $N_2 OP * C_8 H_{11}$
 $N_2 OP * C_{10} H_{13}$
 $N_2 OPSSi * C_{12} H_{31}$
 $N_2 OPSSi_2 * C_{11} H_{31}$
 $N_2 O_2 * CH_4$
 $N_2 O_2 * CH_6$
 $N_2 O_2 * C_7 H_7 Co$
 $N_2 O_2 * C_9 H_{11} Co$
 $N_2 O_2 * C_{11} H_{15} Co$
 $N_2 O_2 OsP_2 * C_{36} H_{30}$
 $N_2 O_2 OsP_2 * C_{36} H_{32} Cl_2$
 $N_2 O_2 P_2 * Cl_4 H_2$
 $N_2 O_2 Re * C_{14} H_9 BF_7$
 $N_2 O_2 Re * C_{14} H_{10} F_3$
 $N_2 O_2 Re * C_{14} H_{12} BF_4$
 $N_2 O_2 Re * C_{14} H_{13}$
 $N_2 O_2 Re * C_{15} H_{15}$
 $N_2 O_2 Re * C_{15} H_{16} BF_4$
 $N_2 O_2 S * H_4$
 $N_2 O_2 Ti * C_4 H_{10}$
 $N_2 O_2 W * C_5 H_5 Cl$
 $N_2 O_2 W * C_5 H_6$
 $N_2 O_4 * C_6 H_{10}$
 $N_2 O_4 P_4 S * C_{52} H_{51} Mo$
 $N_2 O_6 P_2 * K_4$
 $N_2 O_6 S * C_2 H_4$
 $N_2 O_7 * CoH_2$
 $N_2 O_8 Os_3 * C_{20} H_{14}$
 $N_2 O_8 Ru_3 * C_{18} H_{20}$
 $N_2 O_9 * C_{15} H_{16} Fe_3$
 $N_2 O_9 * C_{20} H_{18} Fe_3$
 $N_2 O_{10} * C_{26} H_{40} Cr_2$
 $N_2 O_{10} Os_3 * C_{14} H_6$

$N_2 O_{10} Ru_4 * C_{20} H_{22}$
 $N_2 O_{12} * C_{20} H_{20} Fe_4$
 $N_2 O_{12} * C_{20} H_{20} Fe_5$
 $N_2 O_{18} P_4 Ru_6 * C_{90} H_{60}$
 $N_2 P * C_4 H_{12} Cl$
 $N_2 P * C_5 H_{15}$
 $N_2 P * C_6 H_4 F_7$
 $N_2 P * C_6 H_5 F_6$
 $N_2 P * C_7 H_7 F_6$
 $N_2 P * F_2 H_5$
 $N_2 PS * C_{10} H_{17}$
 $N_2 PS * C_{12} H_{13}$
 $N_2 PSSi_2 * C_{10} H_{27}$
 $N_2 PSi_2 * C_{10} H_{27}$
 $N_2 PSi_3 * C_9 H_{27}$
 $N_2 PSi_3 * C_9 H_{29}$
 $N_2 PW * C_{11} H_{11} F_7$
 $N_2 PW * C_{11} H_{12} F_6$
 $N_2 PW * C_{12} H_{15} F_6$
 $N_2 P_2 * C_2 Cl_6$
 $N_2 P_2 * C_{38} H_{36} B_2 Cu$
 $N_2 P_2 * C_{40} H_{38} BF_4 Ir$
 $N_2 P_2 Pt * C_{18} H_{35} Cl$
 $N_2 P_2 Pt * C_{18} H_{36} Cl_2$
 $N_2 P_2 Rh * C_{24} H_{55}$
 $N_2 P_2 Rh * C_{46} H_{49} Cl$
 $N_2 P_2 Rh * C_{46} H_{51} Cl$
 $N_2 P_2 S_2 * C_{24} H_{22}$
 $N_2 P_3 * C_{24} H_{35} Br_2 Mo$
 $N_2 P_3 * C_{54} H_{46} Co$
 $N_2 P_3 Ru * C_{54} H_{47}$
 $N_2 P_3 W * C_{24} H_{35} Br_2$
 $N_2 P_3 W * C_{24} H_{36} Br_2 Cl$
 $N_2 P_3 W * C_{27} H_{39} Br_2$
 $N_2 P_4 * C_{52} H_{50} Br_2 Mo$
 $N_2 P_4 * C_{53} H_{51} IMo$
 $N_2 P_4 * C_{53} H_{52} BF_4 IMo$
 $N_2 P_4 * C_{56} H_{57} BrMo$
 $N_2 P_4 * C_{57} H_{58} Mo$
 $N_2 P_4 W * C_{52} H_{50} Br_2$
 $N_2 P_4 W * C_{52} H_{51} Br$
 $N_2 P_4 W * C_{53} H_{52} BrCl$
 $N_2 Si_2 Sn * C_{14} H_{36}$
 $N_2 Si_4 Sn * C_{12} H_{36}$
 $N_2 Si_5 * H_{14}$
 $N_2 Sn * C_{10} H_{26}$
 $N_2 Sn * C_{10} H_{27} B$
 $N_2 Sn * C_{12} H_{30}$
 $N_2 Sn * C_{19} H_{38}$
 $N_2 Sn_2 O_4 * C_{18} H_{40}$
 $N_2 Sr * H_4$

N_2Sr_3
 Sr_3N_2
 Hydrolysis to NH_3 : 1.5.3.1.1

$N_2Ti^*C_{10}H_{10}ClMg$
 $N_2Ti^*C_{20}H_{30}$
 $N_2Ti_2^*C_{20}H_{20}ClMg$
 $N_2Ti_2^*C_{20}H_{22}Cl_2$
 $N_2Ti_2^*C_{20}H_{23}$
 $N_2U^*C_{18}H_{30}$
 $N_2Zn^*H_4$
 $N_3^*B_3H_6$
 $N_3^*B_3H_{12}$
 $N_3^*C_3H_9Ge$
 $N_3^*C_4H$
 $N_3^*C_{12}H_9$
 $N_3^*C_{21}H_{18}B$
 N_3^*H
 $N_3^*H_3$
 $N_3^*H_5$
 N_3Na

NaN_3

Reaction with protonic acids: 1.5.3.1.3

$N_3OP^*H_6$
 $N_3O_3^*C_9H_{16}BF_4Mo$
 $N_3O_6^*CH$
 $N_3O_6^*C_6H_{13}ClMo$
 $N_3P^*C_6H_{18}$
 $N_3P^*C_{12}H_{30}$
 $N_3P^*C_{13}H_{15}$
 $N_3P^*C_{18}H_{18}$
 $N_3PSi_4^*C_{10}H_{46}$
 $N_3PSi_5^*C_{15}H_{46}$
 $N_3P_2^*C_{24}H_{23}$
 $N_3P_3^*CH_4Cl_4$
 $N_3P_3^*C_2H_6Cl_4$
 $N_3P_3^*C_3H_8Cl_4$
 $N_3P_3^*C_{25}H_{23}D$
 $N_3P_3^*C_{25}H_{24}$
 $N_3P_3^*C_{25}H_{24}AuCl$
 $N_3P_3^*Cl_6$
 $N_3Si^*C_3H_9$
 $N_3Si_6Th^*C_{18}H_{54}Cl$
 $N_3Si_6Th^*C_{18}H_{55}$
 $N_3Sn^*C_{13}H_{33}$
 $N_3Sn^*C_{14}H_{35}$
 $N_4^*C_8H_{24}Mo$
 $N_4^*C_9H_{22}$
 $N_4^*C_{10}H_{24}$
 $N_4^*C_{11}H_{26}$
 $N_4^*H_4$
 $N_4^*H_6$
 $N_4OOsP^*C_{25}H_{16}ClF_6$

$N_4OOsP^*C_{25}H_{17}F_6$
 $N_4OPRu^*C_{21}H_{17}F_6$
 $N_4O_4^*C_{20}H_{41}ClCo$
 $N_4O_4^*C_{20}H_{42}Co$
 $N_4O_4^*C_{24}H_{24}Mo_2$
 $N_4O_4P^*C_{20}H_{42}Co$
 $N_4O_4PRh^*C_{26}H_{30}$
 $N_4O_4Rh^*C_{26}H_{29}Cl$
 $N_4O_4Rh^*C_{26}H_{30}$
 $N_4O_5Ru^*C_{25}H_{16}Cl_2$
 $N_4O_9S_3^*C_{27}H_{16}F_9Ir$
 $N_4P^*C_8H_{17}$
 $N_4P^*C_9H_{19}$
 $N_4P^*C_{12}H_{25}$
 $N_4P_2^*C_{24}H_{22}$
 $N_4P_2W^*C_{52}H_{48}$
 $N_4P_3^*C_{28}H_{28}Mo$
 $N_4P_3^*C_{42}H_{32}F_{12}Ir$
 $N_4P_4^*C_{32}H_{44}Mo$
 $N_4P_4^*C_{52}H_{48}Mo$
 $N_4P_4^*C_{52}H_{52}Mo$
 $N_4P_4^*C_{60}H_{64}Mo$
 $N_4P_4W^*C_{32}H_{44}$
 $N_4P_4W^*C_{52}H_{48}$
 $N_4P_4W^*C_{52}H_{52}$
 $N_4Si^*C_4H_{10}$
 $N_4Si_4^*C_{12}H_{36}$
 $N_4U^*C_{16}H_{40}$
 $N_4Zn_2^*C_{10}H_{28}$
 $N_5^*C_{25}H_{46}BF_4Fe$
 $N_5O^*C_{25}H_{47}B_2F_8Fe$
 $N_5O_5^*C_{25}H_{45}Fe$
 $N_6^*C_4H_6$
 $N_6O_2P_2S_2^*C_{16}H_{36}Ir_2$
 $N_6O_2P_2S_2^*C_{16}H_{38}Ir_2$
 $N_6O_4^*C_{34}H_{30}Co_2$
 $N_6O_{13}^*C_{43}H_{30}Fe_5$
 $N_6P_2Pt^*C_{36}H_{30}$
 $N_6P_3^*C_6H_{21}$
 $N_6W_2^*C_{12}H_{36}$
 $N_6Zr_2^*C_{40}H_{60}$
 $N_7W^*C_7HK_4$
 $N_7W^*C_7K_5$
Na

Reduction of $CH_3C\equiv CCH_3$: 1.6.3.1.2

Reduction of $C_6H_5CH_2CN$ in liq NH_3 :
 1.6.3.1.2

Na^*AlBH_4
 Na^*AlH_4
 Na^*BD_4
 $Na^*BF_2H_2$
 Na^*BF_3H

Na^*BH_4
 $\text{Na}^*\text{B}_2\text{H}_7$
 $\text{Na}^*\text{B}_{10}\text{H}_{13}$
 $\text{Na}^*\text{CH}_3\text{BN}$
 $\text{Na}^*\text{CH}_{13}\text{B}_{10}$
 $\text{Na}^*\text{C}_2\text{H}_6\text{N}$
 $\text{Na}^*\text{C}_6\text{H}_{15}\text{Ge}$
 $\text{Na}^*\text{C}_6\text{H}_{16}\text{Al}$
 $\text{Na}^*\text{C}_{10}\text{H}_7$
 $\text{Na}^*\text{C}_{10}\text{H}_7$
 $\text{Na}^*\text{C}_{18}\text{H}_{15}\text{Ge}$
 $\text{Na}^*\text{C}_{21}\text{H}_{21}\text{Ge}$
 Na^*Ge
 Na^*GeH_3
 Na^*H
 $\text{Na}^*\text{H}_2\text{N}$
 Na^*Hg
 Na^*I
 Na^*N_3
 $\text{NaNbO}_3^*\text{C}_8\text{H}_6$
 NaO^*CN
 $\text{NaO}^*\text{C}_2\text{H}_8\text{Al}$
 NaO^*H
 NaO_2^*CH
 $\text{NaO}_2^*\text{C}_7\text{H}_5\text{Fe}$
 NaO_2^*Cl
 $\text{NaO}_2^*\text{P}^*\text{H}_2$
 NaO_3^*CH
 $\text{NaO}_3^*\text{C}_3\text{H}_{10}\text{B}$
 $\text{NaO}_3^*\text{C}_8\text{H}_5\text{Mo}$
 NaO_3Si
 NaSiO_3
 Reduction by AlCl_3 - NaCl - H_2 in Al^*
 Cl_3 - NaCl : 1.6.4.2.2
 $\text{NaO}_3\text{Re}^*\text{C}_5$
 $\text{NaO}_6^*\text{C}_3\text{H}_4\text{B}$
 $\text{NaO}_{12}\text{Os}^*\text{C}_{12}\text{Co}_3$
 $\text{NaP}^*\text{C}_{12}\text{H}_{10}$
 NaSi^*H_3
 $\text{NaSi}_2^*\text{C}_6\text{H}_{18}\text{N}$
 $\text{NaSn}^*\text{C}_3\text{H}_9$
 $\text{NaSn}^*\text{C}_6\text{H}_{15}$
 $\text{NaSn}^*\text{C}_{12}\text{H}_{27}$
 $\text{NaSn}^*\text{C}_{18}\text{H}_{15}$
 $\text{NaZn}^*\text{B}_3\text{H}_{12}$
 $\text{NaZn}^*\text{C}_{12}\text{H}_{11}$
 NaZn^*H_3
 $\text{NaZn}_2^*\text{C}_2\text{H}_9$
 Na_2^*C_2
 $\text{Na}_2^*\text{Cl}_6\text{Ir}$
 Na_2^*HN
 $\text{Na}_2\text{NbO}_3^*\text{C}_8\text{H}_5$

$\text{Na}_2\text{O}_3^*\text{Ge}$
 $\text{Na}_2\text{O}_4\text{Os}^*\text{C}_4$
 $\text{Na}_2\text{O}_4\text{P}_2^*\text{H}_2$
 $\text{Na}_2\text{O}_5\text{V}^*\text{C}_5\text{H}$
 $\text{Na}_2\text{O}_6^*\text{Cl}_6\text{H}_{12}\text{Ir}$
 $\text{Na}_2\text{O}_6\text{Os}^*\text{Cl}_6\text{H}_{12}$
 $\text{Na}_2\text{O}_8^*\text{C}_8\text{Fe}_2$
 $\text{Na}_2\text{P}^*\text{C}_6\text{H}_5$
 $\text{Na}_2\text{PS}_3^*\text{H}$
 $\text{Na}_2\text{Re}^*\text{H}_9$
 $\text{Na}_2\text{Zn}_2^*\text{C}_{24}\text{H}_2\text{F}_{20}$
 Na_3^*As
 Na_3^*N
 $\text{Na}_3\text{O}_3^*\text{As}$
 $\text{Na}_3\text{O}_5\text{V}^*\text{C}_5$
 $\text{Na}_3\text{O}_{17}\text{P}_2^*\text{H}_{25}$
 Na_4P_2
 Protonation in liq NH_3 : 1.5.3.2.2
 $\text{Nb}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$
 $\text{Nb}^*\text{C}_{10}\text{H}_{13}$
 $\text{Nb}^*\text{C}_{10}\text{H}_{14}\text{B}$
 Nb^*Cl_5
 Nb^*H
 Nb^*H_2
 $\text{NbO}^*\text{C}_{11}\text{H}_{11}$
 $\text{NbO}_3^*\text{C}_8\text{H}_5\text{Na}_2$
 $\text{NbO}_3^*\text{C}_8\text{H}_6\text{Na}$
 $\text{NbO}_3^*\text{C}_{26}\text{H}_{20}$
 $\text{NbO}_4^*\text{C}_9\text{H}_5$
 $\text{NbP}^*\text{C}_{18}\text{H}_{22}$
 Nb_2^*C
 $\text{Nb}_6^*\text{HI}_{11}$
 $\text{Nb}_6^*\text{I}_{11}$
 $\text{Nb}_{21}\text{S}_8^*\text{H}_5$
 $\text{Nd}^*\text{C}_{15}\text{H}_{15}$
 Nd^*Co_5
 Nd^*Fe_2
 Nd^*H_2
 Nd^*Mg_2
 NdNi_2
 Reaction with H_2 : 1.12.8.1.2
 NdNi_5
 Reaction with H_2 : 1.12.8.1.1
 NdRu_2
 Reaction with H_2 : 1.12.8.1.2
 Ni
 Catalysis for H_2 reaction with graphite:
 1.6.2.1.1
 Catalysis for alkane exchange with D_2 :
 1.6.7.2.1
 Catalysis of CO reaction with H_2 :
 1.6.6.1

$\text{Ni}^*\text{C}_{20}\text{H}_{30}$
 Ni^*H
 Ni^*Hf
 Ni^*Mg_2
 $\text{NiOP}_2^*\text{C}_{42}\text{H}_{72}$
 $\text{NiO}_9\text{Ru}_3^*\text{C}_{14}\text{H}_8$
 $\text{NiO}_{12}\text{P}_4^*\text{C}_{24}\text{H}_{60}$
 $\text{NiP}^*\text{C}_{21}\text{H}_{20}\text{Br}$
 $\text{NiP}^*\text{C}_{23}\text{H}_{21}$
 $\text{NiPSi}_2^*\text{C}_{11}\text{H}_{23}$
 $\text{NiP}_2^*\text{C}_{36}\text{H}_{66}$
 $\text{NiP}_2^*\text{C}_{36}\text{H}_{66}\text{Cl}_2$
 $\text{NiP}_2^*\text{C}_{36}\text{H}_{67}\text{Cl}$
 $\text{NiP}_2^*\text{C}_{40}\text{H}_{71}\text{N}$
 $\text{NiP}_3^*\text{C}_{66}\text{H}_{55}\text{DGe}$
 $\text{NiP}_3^*\text{C}_{66}\text{H}_{56}\text{Ge}$
 $\text{NiPt}_4^*\text{C}_{52}\text{H}_{48}$
 NiTi
 Reaction with H_2 : 1.12.8.1.3
 NiZr
 Reaction with H_2 : 1.12.8.1.3
 $\text{Ni}_2^*\text{C}_{16}\text{H}_{24}\text{Cl}_4$
 $\text{Ni}_2^*\text{C}_{56}\text{H}_{40}\text{Br}_4$
 Ni_2^*Ce
 Ni_2^*Dy
 Ni_2^*Er
 Ni_2^*Eu
 Ni_2^*Gd
 Ni_2^*Ho
 Ni_2^*La
 Ni_2^*Nd
 $\text{Ni}_2\text{O}_2^*\text{C}_{12}\text{H}_{10}$
 $\text{Ni}_2\text{P}_2\text{Si}_4^*\text{C}_{22}\text{H}_{46}$
 Ni_2Pr
 PrNi_2
 Reaction with H_2 : 1.12.8.1.2
 Ni_2Sc
 ScNi_2
 Reaction with H_2 : 1.12.8.1.2
 $\text{Ni}_3\text{P}_3^*\text{C}_{15}\text{H}_{15}\text{D}_6$
 $\text{Ni}_3\text{P}_3^*\text{C}_{15}\text{H}_{21}$
 Ni_5^*Ce
 Ni_5^*Eu
 $\text{Ni}_5^*\text{H}_6\text{La}$
 Ni_5^*La
 Ni_5^*Nd
 Ni_5Pr
 PrNi_5
 Reaction with H_2 : 1.12.8.1.1
 Ni_5Sm
 SmNi_5
 Reaction with H_2 : 1.12.8.1.1

Ni_5Y
 YNi_5
 Reaction with H_2 : 1.12.8.1.1
 Ni_5Yb
 YbNi_5
 Reaction with H_2 : 1.12.8.1.1
 O^*C
 O^*CAuCl
 O^*CF_2
 O^*CHK
 O^*CHN
 O^*CH_2
 O^*CH_4
 $\text{O}^*\text{CH}_4\text{AlLi}$
 $\text{O}^*\text{CH}_4\text{N}_2$
 O^*CNNa
 $\text{O}^*\text{C}_2\text{H}_3\text{Cl}$
 $\text{O}^*\text{C}_2\text{H}_4$
 $\text{O}^*\text{C}_2\text{H}_5\text{D}$
 $\text{O}^*\text{C}_2\text{H}_6$
 $\text{O}^*\text{C}_2\text{H}_7\text{As}$
 $\text{O}^*\text{C}_2\text{H}_8\text{AlNa}$
 $\text{O}^*\text{C}_3\text{H}_5\text{D}_3$
 $\text{O}^*\text{C}_3\text{H}_6$
 $\text{O}^*\text{C}_3\text{H}_6\text{D}_2$
 $\text{O}^*\text{C}_3\text{H}_8$
 $\text{O}^*\text{C}_4\text{H}_4$
 $\text{O}^*\text{C}_4\text{H}_8$
 $\text{O}^*\text{C}_4\text{H}_{10}$
 $\text{O}^*\text{C}_4\text{H}_{11}\text{Cl}_3\text{Ge}$
 $\text{O}^*\text{C}_5\text{H}_{10}$
 $\text{O}^*\text{C}_5\text{H}_{12}$
 $\text{O}^*\text{C}_6\text{H}_5\text{N}$
 $\text{O}^*\text{C}_7\text{H}_5\text{D}_3$
 $\text{O}^*\text{C}_7\text{H}_5\text{N}$
 $\text{O}^*\text{C}_7\text{H}_6$
 $\text{O}^*\text{C}_7\text{H}_6\text{D}_2$
 $\text{O}^*\text{C}_7\text{H}_7\text{N}$
 $\text{O}^*\text{C}_7\text{H}_8$
 $\text{O}^*\text{C}_7\text{H}_9\text{As}$
 $\text{O}^*\text{C}_7\text{H}_{16}$
 $\text{O}^*\text{C}_8\text{H}_8$
 $\text{O}^*\text{C}_8\text{H}_8\text{D}_2$
 $\text{O}^*\text{C}_8\text{H}_9\text{N}$
 $\text{O}^*\text{C}_8\text{H}_{10}$
 $\text{O}^*\text{C}_9\text{H}_{12}\text{Fe}$
 $\text{O}^*\text{C}_{11}\text{H}_{11}\text{Nb}$
 $\text{O}^*\text{C}_{11}\text{H}_{15}\text{N}$
 $\text{O}^*\text{C}_{14}\text{H}_{14}\text{N}_2$
 $\text{O}^*\text{C}_{15}\text{H}_{17}\text{As}$
 $\text{O}^*\text{C}_{18}\text{H}_{16}\text{Ge}$
 $\text{O}^*\text{C}_{18}\text{H}_{21}\text{Al}$

OP*C ₁₉ H ₁₇ As	OP*C ₂₉ H ₃₅ B ₁₀ IrN
OP*C ₂₅ H ₄₇ B ₂ F ₈ FeN ₅	OP*C ₃₄ H ₃₅ B ₁₀ IrN
OP*C ₃₆ H ₃₀ Ge ₂	OP*C ₃₄ H ₃₇ B ₁₀ IrN
OP*C ₃₇ H ₃₀ As ₂ ClIr	OP*Cl ₃
OP*D ₂	OP*H ₆ N ₃
OP*Ge	OPPt*C ₁₇ H ₃₈ BF ₄
OPGe*C ₄ H ₁₁ Cl ₃	OPPt*C ₂₇ H ₂₆ Cl ₂ N
OP*GeH ₂	OPRe*C ₂₃ H ₂₁ N
OP*Ge ₂ H ₆	OPRh ₃ *C ₃₀ H ₄₈ F ₆
OP*HNa	OPRu*C ₂₁ H ₁₇ F ₆ N ₄
OP*H ₂	OPSS*C ₁₄ H ₁₆ N
OP*H ₃ N	OPSSi*C ₁₂ H ₃₁ N ₂
OP*N	OPSSi*C ₁₁ H ₃₁ N ₂
OP*N ₂	OPSi*C ₁₁ H ₂₇
OOs*C ₁₁ H ₁₈	OP ₂ *C ₇ H ₁₈ ClIr
OOsP*C ₂₅ H ₁₆ ClF ₆ N ₄	OP ₂ *C ₁₃ H ₃₀ ClIr
OOsP*C ₂₅ H ₁₇ F ₆ N ₄	OP ₂ *C ₁₉ H ₄₂ BrIr
OOsP ₃ *C ₅₅ H ₄₆ Cl	OP ₂ *C ₁₉ H ₄₂ ClIr
OOsP ₃ *C ₅₅ H ₄₇	OP ₂ *C ₁₉ H ₄₂ IIr
OP*Br ₃	OP ₂ *C ₂₇ H ₂₄ D ₃ Ir
OP*C ₂ H ₇	OP ₂ *C ₂₇ H ₂₅ Ir
OP*C ₅ H ₁₀ Cl	OP ₂ *C ₂₇ H ₂₇ Ir
OP*C ₅ H ₁₀ F ₂	OP ₂ *C ₂₉ H ₃₇ B ₁₀ Ir
OP*C ₅ H ₁₁	OP ₂ *C ₂₉ H ₃₉ B ₁₀ Ir
OP*C ₆ H ₅ Cl ₂	OP ₂ *C ₃₀ H ₃₉ B ₁₀ Ir
OP*C ₆ H ₅ F	OP ₂ *C ₃₀ H ₄₁ B ₁₀ Ir
OP*C ₇ H ₉	OP ₂ *C ₃₃ H ₃₈ ClIr
OP*C ₇ H ₉ F ₂	OP ₂ *C ₃₅ H ₃₉ B ₁₀ Ir
OP*C ₈ H ₈ F ₅	OP ₂ *C ₃₅ H ₄₁ B ₁₀ Ir
OP*C ₈ H ₁₀ N	OP ₂ *C ₃₅ H ₄₃ B ₁₀ Ir
OP*C ₈ H ₁₁ F ₂	OP ₂ *C ₃₆ H ₃₃ Cl ₃ IrN
OP*C ₈ H ₁₁ N ₂	OP ₂ *C ₃₇ H ₃₀ BrIr
OP*C ₈ H ₁₈ Cl	OP ₂ *C ₃₇ H ₃₀ ClIr
OP*C ₉ H ₇ F ₈	OP ₂ *C ₃₇ H ₃₀ IIr
OP*C ₁₀ H ₁₀ Cl	OP ₂ *C ₃₇ H ₃₁ Cl ₂ Ir
OP*C ₁₀ H ₁₃ N ₂	OP ₂ *C ₃₇ H ₃₁ D ₂ Ir
OP*C ₁₀ H ₁₄ Cl	OP ₂ *C ₃₇ H ₃₁ Ir
OP*C ₁₀ H ₁₅	OP ₂ *C ₃₇ H ₃₂ ClIr
OP*C ₁₁ H ₁₆ N	OP ₂ *C ₃₇ H ₃₃ Ir
OP*C ₁₂ H ₁₀ Cl	OP ₂ *C ₃₇ H ₃₈ B ₃ Ir
OP*C ₁₂ H ₁₁	OP ₂ *C ₃₇ H ₆₆ BrIr
OP*C ₁₄ H ₁₂ F ₅	OP ₂ *C ₃₇ H ₆₆ ClIr
OP*C ₁₄ H ₁₄ Cl	OP ₂ *C ₃₇ H ₆₆ IIr
OP*C ₁₄ H ₁₅ BCl ₃	OP ₂ *C ₃₉ H ₄₁ B ₁₀ Ir
OP*C ₁₄ H ₁₆ N	OP ₂ *C ₃₉ H ₄₃ B ₁₀ Ir
OP*C ₁₄ H ₂₉	OP ₂ *C ₄₀ H ₄₃ B ₁₀ Ir
OP*C ₁₄ H ₃₀	OP ₂ *C ₄₀ H ₄₅ B ₁₀ Ir
OP*C ₁₉ H ₁₅	OP ₂ *C ₄₂ H ₇₂ Ni
OP*C ₁₉ H ₁₅ ClIr	OP ₂ *C ₄₃ H ₄₂ ClIr
OP*C ₂₅ H ₂₂ Mn	OP ₂ *C ₄₅ H ₄₅ B ₁₀ Ir
OP*C ₂₅ H ₂₃ Mn	OP ₂ *C ₄₅ H ₄₇ B ₁₀ Ir
OP*C ₂₉ H ₃₃ B ₁₀ IrN	

$\text{OP}_2^*\text{Cl}_5\text{N}$
 $\text{OP}_2\text{Pt}^*\text{C}_{13}\text{H}_{30}\text{BClF}_4$
 $\text{OP}_2\text{Pt}^*\text{C}_{18}\text{H}_{44}$
 $\text{OP}_2\text{Pt}^*\text{C}_{19}\text{H}_{36}\text{ClN}$
 $\text{OP}_2\text{Pt}^*\text{C}_{19}\text{H}_{39}\text{BF}_4$
 $\text{OP}_2\text{Pt}^*\text{C}_{22}\text{H}_{26}\text{BF}_4$
 $\text{OP}_2\text{Pt}^*\text{C}_{43}\text{H}_{36}\text{ClN}$
 $\text{OP}_3\text{Re}^*\text{C}_{20}\text{H}_{30}\text{Cl}_3$
 $\text{OP}_2\text{Rh}^*\text{C}_{37}\text{H}_{30}\text{Cl}$
 $\text{OP}_2\text{Rh}^*\text{C}_{40}\text{H}_{37}$
 $\text{OP}_3^*\text{C}_{39}\text{H}_{41}\text{B}_{10}\text{Ir}$
 $\text{OP}_3^*\text{C}_{54}\text{H}_{45}\text{IrN}$
 $\text{OP}_3^*\text{C}_{55}\text{H}_{46}\text{Ir}$
 $\text{OP}_3\text{Rh}^*\text{C}_{55}\text{H}_{46}$
 $\text{OP}_3\text{Ru}^*\text{C}_{31}\text{H}_{46}\text{Cl}$
 $\text{OP}_3\text{Ru}^*\text{C}_{54}\text{H}_{46}\text{N}$
 $\text{OP}_3\text{Ru}^*\text{C}_{55}\text{H}_{47}$
 $\text{OP}_4^*\text{C}_{13}\text{H}_{32}\text{ClIr}$
 $\text{OP}_4\text{Pt}_2^*\text{C}_{51}\text{H}_{45}$
 $\text{OP}_5^*\text{C}_{13}\text{H}_{38}\text{F}_6\text{Ir}$
 $\text{OP}_5\text{Pt}_2^*\text{C}_{51}\text{H}_{45}\text{F}_6$
 $\text{OP}_6\text{Ru}_2^*\text{C}_{18}\text{H}_{56}$
OPdZr₂
 PdZr₂O

Reaction with H_2 : 1.12.8.2.3

$\text{OPTSP}_2^*\text{C}_{38}\text{H}_{34}$
 $\text{ORhSi}^*\text{C}_{24}\text{H}_{21}$
 $\text{ORu}^*\text{Cl}_3\text{N}$

OSi

SiO

Reaction with dil aq HF: 1.6.3.2.1

OSi^*CH_4
 $\text{OSi}^*\text{C}_2\text{H}_6\text{Cl}_2$
 $\text{OSi}^*\text{C}_2\text{H}_8$
 $\text{OSi}^*\text{C}_3\text{H}_{10}$
 $\text{OSi}^*\text{C}_4\text{H}_{12}$
 $\text{OSi}^*\text{C}_6\text{H}_{16}$
 $\text{OSi}^*\text{C}_{11}\text{H}_{26}$
 $\text{OSi}^*\text{C}_{31}\text{H}_{25}\text{Li}$
 $\text{OSi}^*\text{C}_{31}\text{H}_{26}$
 $\text{OSi}_2^*\text{C}_4\text{H}_{14}$
 $\text{OSi}_2^*\text{C}_6\text{H}_{18}$
 $\text{OSi}_2^*\text{C}_{24}\text{H}_{22}$
 $\text{OSi}_2^*\text{Cl}_6$
 OSi_2^*H_6
 $\text{OSn}^*\text{C}_8\text{H}_{18}$
 $\text{OSn}^*\text{C}_{13}\text{H}_{21}\text{N}$
 $\text{OSn}^*\text{C}_{25}\text{H}_{22}$
 $\text{OSn}_2^*\text{C}_{24}\text{H}_{54}$
 $\text{OTa}^*\text{C}_{11}\text{H}_{11}$
 $\text{OTl}^*\text{C}_2\text{H}_5$

OV₃Zr₃

Zr₃V₃O

Reaction with H_2 : 1.12.8.2.3

$\text{OW}^*\text{C}_{11}\text{H}_{10}$

$\text{OWZr}^*\text{C}_{31}\text{H}_{42}$

$\text{O}_x\text{Ti}_4^*\text{Fe}_2$

OZn

ZnO

Chemisorption medium for H_2 : 1.9.5.2

$\text{OZr}^*\text{C}_{11}\text{H}_{11}\text{Cl}$

$\text{OZr}^*\text{C}_{11}\text{H}_{14}$

$\text{OZr}^*\text{C}_{21}\text{H}_{32}$

$\text{OZr}^*\text{C}_{21}\text{H}_{34}$

O₂

Impurity in H_2 : 1.8.2

Poison for hydriding reaction: 1.12.8.1.1

O_2^*B_2

O_2^*C

O_2^*CHK

O_2^*CHLi

O_2^*CHNa

O_2^*CH_2

$\text{O}_2^*\text{CH}_4\text{Ge}$

$\text{O}_2^*\text{CH}_4\text{N}_2$

$\text{O}_2^*\text{CH}_6\text{N}_2$

$\text{O}_2^*\text{C}_2\text{HF}_3$

$\text{O}_2^*\text{C}_2\text{H}_4$

$\text{O}_2^*\text{C}_2\text{H}_5\text{N}$

$\text{O}_2^*\text{C}_2\text{H}_6$

$\text{O}_2^*\text{C}_2\text{H}_6\text{AgB}$

$\text{O}_2^*\text{C}_2\text{H}_6\text{BCl}$

$\text{O}_2^*\text{C}_2\text{H}_7\text{As}$

$\text{O}_2^*\text{C}_2\text{H}_7\text{B}$

$\text{O}_2^*\text{C}_2\text{H}_8\text{B}_{10}$

O_2^*C_3

$\text{O}_2^*\text{C}_3\text{H}_5\text{N}$

$\text{O}_2^*\text{C}_4\text{H}_4\text{BrN}$

$\text{O}_2^*\text{C}_4\text{H}_5\text{N}$

$\text{O}_2^*\text{C}_4\text{H}_7$

$\text{O}_2^*\text{C}_4\text{H}_8$

$\text{O}_2^*\text{C}_4\text{H}_9\text{N}$

$\text{O}_2^*\text{C}_6\text{H}_5\text{N}$

$\text{O}_2^*\text{C}_6\text{H}_6$

$\text{O}_2^*\text{C}_6\text{H}_7\text{As}$

$\text{O}_2^*\text{C}_6\text{H}_{11}\text{N}$

$\text{O}_2^*\text{C}_6\text{H}_{15}\text{N}$

$\text{O}_2^*\text{C}_7\text{H}_5\text{FeNa}$

$\text{O}_2^*\text{C}_7\text{H}_6$

$\text{O}_2^*\text{C}_7\text{H}_6\text{Fe}$

$\text{O}_2^*\text{C}_7\text{H}_7\text{CoN}_2$

$\text{O}_2^*\text{C}_7\text{H}_9\text{As}$

$\text{O}_2^*\text{C}_8\text{H}_8\text{Hg}$

- $O_2^*C_9H_6F_4Fe$
 $O_2^*C_9H_{11}CoN_2$
 $O_2^*C_{10}H_9FeN$
 $O_2^*C_{10}H_{10}Fe$
 $O_2^*C_{10}H_{10}FeN$
 $O_2^*C_{10}H_{11}ClFe$
 $O_2^*C_{11}H_{15}CoN_2$
 $O_2^*C_{12}H_{10}Ni_2$
 $O_2^*C_{12}H_{12}Mo$
 $O_2^*C_{12}H_{13}Ir$
 $O_2^*C_{12}H_{16}BF_4Ir$
 $O_2^*C_{16}H_{15}Ir$
 $O_2^*C_{16}H_{34}Ge$
 $O_2^*C_{18}H_{15}B$
 O_2^*ClNa
 O_2^*Ge
 $O_2^*GeH_2$
 O_2^*HN
 $O_2Os^*C_{12}H_{16}$
 $O_2OsP_2^*C_{36}H_{30}N_2$
 $O_2OsP_2^*C_{36}H_{32}Cl_2N_2$
 $O_2OsP_2^*C_{37}H_{30}ClN$
 $O_2OsP_2^*C_{37}H_{31}Cl_2N$
 $O_2OsP_3^*C_{56}H_{45}$
 $O_2Os_2^*C_{22}H_{30}$
 $O_2Os_2^*C_{22}H_{32}$
 $O_2P^*CH_2F_3$
 $O_2P^*CH_4$
 $O_2P^*CH_5$
 $O_2P^*C_2H_6Cl$
 $O_2P^*C_2H_7$
 $O_2P^*C_3H_9$
 $O_2P^*C_4H_{11}$
 $O_2P^*C_5H_{11}$
 $O_2P^*C_6H_7$
 $O_2P^*C_6H_{15}$
 $O_2P^*C_7H_9$
 $O_2P^*C_8H_{11}$
 $O_2P^*C_8H_{19}$
 $O_2P^*C_{10}H_{14}N$
 $O_2P^*C_{10}H_{16}N$
 $O_2P^*C_{12}H_{11}$
 $O_2P^*C_{12}H_{23}$
 $O_2P^*C_{13}H_{13}$
 $O_2P^*C_{14}H_{13}$
 $O_2P^*C_{14}H_{15}$
 $O_2P^*C_{14}H_{16}N$
 $O_2P^*C_{15}H_{16}Mn$
 $O_2P^*C_{18}H_{15}$
 $O_2P^*C_{18}H_{20}Li$
 $O_2P^*C_{18}H_{21}$
 $O_2P^*C_{25}H_{20}ClFe$
 $O_2P^*C_{25}H_{20}Re$
 $O_2P^*C_{26}H_{21}Cr$
 $O_2P^*C_{26}H_{41}Fe$
 $O_2P^*C_{26}H_{42}BF_4Fe$
 $O_2P^*C_{28}H_{21}IrN$
 $O_2P^*C_{28}H_{22}ClIrN$
 $O_2P^*C_{28}H_{32}B_{10}Ir$
 $O_2P^*H_2Na$
 $O_2P^*H_3$
 $O_2PRe^*C_{25}H_{20}$
 $O_2PS_2^*C_4H_{11}$
 $O_2PS_2Si^*C_{12}H_{29}$
 $O_2PSn^*C_{12}H_{21}$
 $O_2PSn^*C_{15}H_{27}$
 $O_2PW^*C_{10}H_{15}$
 $O_2P_2^*C_{26}H_{26}BCu$
 $O_2P_2^*C_{36}H_{36}BF_4Ir$
 $O_2P_2^*C_{38}H_{31}Ir$
 $O_2P_2^*C_{38}H_{40}BF_4Ir$
 $O_2P_2^*C_{40}H_{44}BF_4Ir$
 $O_2P_2^*C_{42}H_{44}BF_4Ir$
 $O_2P_2^*C_{42}H_{48}BF_4Ir$
 $O_2P_2^*C_{44}H_{48}BF_4Ir$
 $O_2P_2^*C_{44}H_{52}BF_4Ir$
 $O_2P_2^*Cl_4H_2N_2$
 $O_1P_2Pd^*C_{20}H_{43}F_3$
 $O_2P_2Pt^*C_{13}H_{31}Cl$
 $O_2P_2Ru^*C_{36}H_{34}$
 $O_2P_2Ru^*C_{38}H_{32}$
 $O_2P_2S_2^*C_{16}H_{36}Ir_2$
 $O_2P_2S_2^*C_{16}H_{36}Ir_2N_6$
 $O_2P_2S_2^*C_{16}H_{38}Ir_2$
 $O_2P_2S_2^*C_{16}H_{38}Ir_2N_6$
 $O_2P_2S_2^*C_{46}H_{48}Ir_2$
 $O_2P_2S_2^*C_{46}H_{50}Ir_2$
 $O_2P_2V^*C_{43}H_{39}BN$
 $O_2P_3^*C_{42}H_{47}AgB$
 $O_2P_3^*C_{56}H_{51}AgB$
 $O_2P_3^*C_{56}H_{51}BCu$
 $O_2P_3Pt^*C_{42}H_{37}$
 $O_2P_3Ru^*C_{56}H_{49}$
 $O_2P_4^*C_{57}H_{56}Mo$
 $O_2P_4Pt_2^*C_{62}H_{44}$
 $O_2Pb^*C_{14}H_{30}$
 $O_2Pt^*C_{26}H_{55}As_2F_3$
 $O_2Pt_2^*C_{32}H_{30}F_8$
 $O_2Pt_2^*C_{33}H_{31}BF_{12}$
 $O_2Re^*C_6H_6N$
 $O_2Re^*C_7H_7$
 $O_2Re^*C_7H_8N$
 $O_2Re^*C_{14}H_9BF_7N_2$
 $O_2Re^*C_{14}H_{10}F_3N_2$

- $O_2Re^*C_{14}H_{12}BF_4N_2$
 $O_2Re^*C_{14}H_{13}N_2$
 $O_2Re^*C_{15}H_{15}N_2$
 $O_2Re^*C_{15}H_{16}BF_4N_2$
 $O_2ReSi^*C_{25}H_{21}$
 $O_2Rh^*C_7H_5$
 $O_2Rh^*C_{12}H_{15}$
 $O_2Rh^*C_{18}H_{20}B$
 $O_2Ru^*C_7H_6$
 $O_2Ru^*C_{12}H_{15}K$
 $O_2Ru^*C_{12}H_{16}$
 $O_2Ru_2^*C_{15}H_{16}$
 $O_2S^*H_4N_2$
 O_2Se
 SeO_2
 Reaction with aq P_4 : 1.5.3.2.1
 O_2Si
 SiO_2
 Reaction with $Li[AlH_4]$: 1.6.5.2.2
 Reaction with H_2 over Al and $AlCl_3$:
 1.6.2.2
 $O_2Si^*C_2H_7Cl$
 $O_2Si^*C_2H_8$
 $O_2Si^*C_4H_{10}Cl_2$
 $O_2Si^*C_4H_{10}F_2$
 $O_2Si^*C_4H_{11}Cl$
 $O_2Si^*C_4H_{12}$
 $O_2Si^*C_6H_{16}$
 $O_2Si^*C_8H_{20}$
 $O_2Si^*C_{16}H_{20}$
 $O_2Si^*C_{20}H_{18}ClMn$
 $O_2Si^*C_{25}H_{23}Mn$
 O_2Si^*Ge
 $O_2Sn^*CH_3K$
 $O_2Sn^*C_4H_{12}$
 $O_2Sn^*C_6H_{16}$
 $O_2Sn^*C_8H_{20}$
 $O_2Sn^*C_{13}H_{28}$
 $O_2Sn^*C_{14}H_{16}$
 O_2Ti
 TiO_2
 Precipitation from $TiFe$: 1.12.8.1.3
 Reduction with B_4C : 1.7.2
 $O_2Ti^*C_4H_{10}$
 $O_2Ti^*C_4H_{10}N_2$
 $O_2Ti^*C_{12}H_{10}$
 $O_2V^*H_2$
 $O_2W^*C_5H_5ClN_2$
 $O_2W^*C_5H_6N_2$
 $O_2W^*C_{18}H_{18}$
 $O_2Zn^*C_8H_{34}B_{12}$
 $O_2Zr^*C_{12}H_{10}$
 $O_2Zr^*C_{22}H_{30}$
 $O_3^*AcH_3$
 $O_3^*AsNa_3$
 $O_3^*BH_3$
 $O_3^*B_2$
 $O_3^*B_3H_3$
 O_3^*CHNa
 $O_3^*C_3H_9B$
 $O_3^*C_3H_9B_5Fe$
 $O_3^*C_3H_{10}B$
 $O_3^*C_3H_{10}BLi$
 $O_3^*C_3H_{10}BNa$
 $O_3^*C_7H_4ClN$
 $O_3^*C_7H_5N$
 $O_3^*C_7H_6Fe$
 $O_3^*C_7H_7ClFe$
 $O_3^*C_7H_{16}$
 $O_3^*C_8H_5ClMo$
 $O_3^*C_8H_5MoNa$
 $O_3^*C_8H_5Na_2Nb$
 $O_3^*C_8H_6Cr$
 $O_3^*C_8H_6Mo$
 $O_3^*C_8H_6NaNb$
 $O_3^*C_8H_8Fe$
 $O_3^*C_9CrD_6$
 $O_3^*C_9H_6Cr$
 $O_3^*C_9H_7Mn$
 $O_3^*C_9H_{16}BF_4MoN_3$
 $O_3^*C_9H_{21}B$
 $O_3^*C_9H_{22}BK$
 $O_3^*C_{11}H_8Mo$
 $O_3^*C_{12}H_{12}Cr$
 $O_3^*C_{12}H_{28}AlLi$
 $O_3^*C_{15}H_{14}Fe_2$
 $O_3^*C_{18}H_{15}B$
 $O_3^*C_{26}H_{20}Nb$
 $O_3^*GeNa_2$
 O_3^*Mo
 $O_3OsP_2^*C_{39}H_{30}$
 $O_3P^*C_2H_7$
 $O_3P^*C_3H_9$
 $O_3P^*C_4H_{11}$
 $O_3P^*C_5H_{13}$
 $O_3P^*C_6H_7$
 $O_3P^*C_6H_9$
 $O_3P^*C_6H_{12}N$
 $O_3P^*C_6H_{13}BF_4N$
 $O_3P^*C_6H_{15}$
 $O_3P^*C_7H_{17}$
 $O_3P^*C_8H_5F_6Mo$
 $O_3P^*C_8H_{10}N$
 $O_3P^*C_8H_{11}$

$O_3P^*C_8H_{19}$
 $O_3P^*C_9H_{21}$
 $O_3P^*C_{10}H_{14}N$
 $O_3P^*C_{10}H_{15}$
 $O_3P^*C_{11}H_{14}N$
 $O_3P^*C_{11}H_{17}$
 $O_3P^*C_{12}H_{11}$
 $O_3P^*C_{12}H_{15}$
 $O_3P^*C_{12}H_{16}N$
 $O_3P^*C_{12}H_{18}N$
 $O_3P^*C_{12}H_{23}$
 $O_3P^*C_{12}H_{27}$
 $O_3P^*C_{18}H_{15}$
 $O_3P^*C_{21}H_{16}Co$
 $O_3P^*C_{25}H_{21}Fe$
 $O_3P^*C_{29}H_{30}B_{10}Ir$
 $O_3P^*C_{29}H_{32}B_{10}Ir$
 $O_3P^*D_3$
 $O_3P^*H_3$
 $O_3PRe^*C_7H_5F_6N$
 $O_3PRe^*C_{24}H_{21}N$
 $O_3PRh_2^*C_{20}H_{33}F_6$
 $O_3P_2^*C_{11}H_{18}$
 $O_3P_2^*C_{18}H_{24}$
 $O_3P_2Rh^*C_{19}H_{45}$
 $O_3P_3^*C_{12}H_{21}Mo$
 $O_3P_3^*C_{39}H_{30}F_6Ir$
 $O_3-Pd^*La_2$
 $O_3Re^*C_7H_6N$
 $O_3Re^*C_7H_8N$
 $O_3Re^*C_8H_5$
 $O_3Re^*C_9H_9$
 $O_3Re^*C_{15}H_{19}$
 $O_3Rh_2^*C_{13}H_{10}$
 $O_3Rh_2^*C_{13}H_{11}Br_4$
 $O_3Rh_2^*C_{23}H_{31}BF_4$
 $O_3Ru_2^*C_{14}H_{12}$
 $O_3Ru_2^*C_{15}H_{14}$
 $O_3Ru_2^*C_{16}H_{14}$
 $O_3Ru_2^*C_{16}H_{15}BF_4$
 $O_3Ru_3^*C_{18}H_{18}$
 $O_3S^*H_3N$
 O_3Sb_2
 Sb_2O_3

Reduction by $LiAlH_4$: 1.5.5.4

O_3Si^*Na
 $O_3Si_4Sn^*C_{22}H_{44}Mo$
 $O_3Si_6^*H_6$
 $O_3Sn^*C_{10}H_{22}$
 $O_3V^*C_{26}H_{20}$
 $O_3V^*C_{44}H_{36}N$
 O_3W

WO_3

Formation of hydride: 1.12.8.2.3

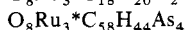
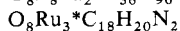
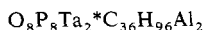
$O_3W^*C_8H_6$
 $O_3-Zn^*Cr_2$
 $O_4^*C_2H_4AlLi$
 $O_4^*C_2H_4BLi$
 $O_4^*C_4HCo$
 $O_4^*C_4HFeK$
 $O_4^*C_4H_2Fe$
 $O_4^*C_4H_{12}AlLi$
 $O_4^*C_5H_4As$
 $O_4^*C_6H_{10}N_2$
 $O_4^*C_7H_9As$
 $O_4^*C_8H_6Fe$
 $O_4^*C_8H_7ClFe$
 $O_4^*C_9H_5Nb$
 $O_4^*C_{14}H_{10}Cl_2Fe_2Ge$
 $O_4^*C_{14}H_{10}Fe_2$
 $O_4^*C_{14}H_{12}Fe_2Ge$
 $O_4^*C_{14}H_{15}N$
 $O_4^*C_{14}H_{17}N$
 $O_4^*C_{16}H_{36}Zr$
 $O_4^*C_{18}H_{40}N_2Sn_2$
 $O_4^*C_{20}H_{41}ClCoN_4$
 $O_4^*C_{20}H_{42}CoN_4$
 $O_4^*C_{24}H_{24}Mo_2N_4$
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 O_4^*ClH
 $O_4^*H_2S$
 O_4Os

OsO_4

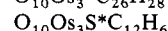
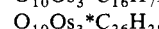
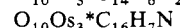
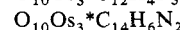
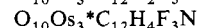
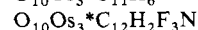
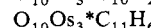
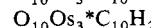
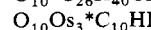
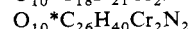
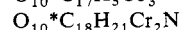
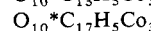
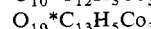
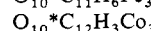
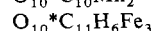
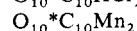
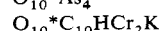
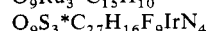
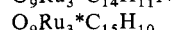
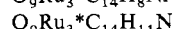
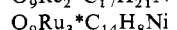
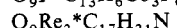
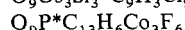
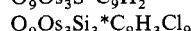
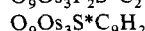
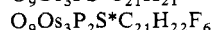
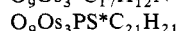
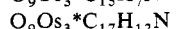
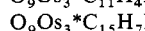
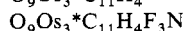
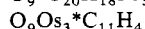
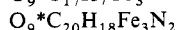
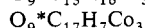
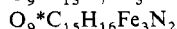
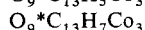
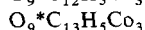
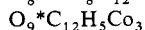
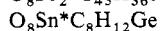
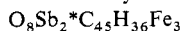
Reaction with CO and H_2 : 1.10.3.1

$O_4Os^*C_4H_2$
 $O_4Os^*C_4Na_2$
 $O_4Os^*C_5H_4$
 $O_4P^*C_6H_9MoN$
 $O_4P^*C_{12}H_{15}$
 $O_4P^*C_{14}H_{10}ClD_2Fe_2$
 $O_4P^*C_{14}H_{11}F_6Fe_2$
 $O_4P^*C_{14}H_{12}ClFe_2$
 $O_4P^*C_{20}H_{42}CoN_4$
 $O_4P^*C_{22}H_{16}Mn$
 $O_4P^*H_3$
 $O_4PRh^*C_{26}H_{30}N_4$
 $O_4PS^*C_{12}H_8Cl_2N$
 $O_4PSi^*C_{16}H_{28}$
 $O_4P_2^*BaD_4$
 $O_4P_2^*BaH_2$
 $O_4P_2^*BaH_4$
 $O_4P_2^*C_{26}H_{22}Mn_2$
 $O_4P_2^*C_{40}H_{31}FeN$
 $O_4P_2^*C_{40}H_{33}Ir$
 $O_4P_2^*H_2Na_2$
 $O_4P_3^*C_{52}H_{40}FeIr$
 $O_4P_3^*C_{52}H_{44}FeIr$
 $O_4P_4Rh^*C_{62}H_{64}BF_4$

$O_4P_4Rh^*C_{62}H_{66}BF_4$	$O_5V^*C_{13}H_{24}Cl_2Mg_2N$
$O_4P_4S^*C_{52}H_{51}MoN_2$	$O_5W^*C_{10}H_5F_3$
$O_4Re^*C_7H_6N$	$O_6^*As_4$
$O_4Rh^*C_{15}H_{12}$	$O_6^*CHN_3$
$O_4Rh^*C_{26}H_{29}ClN_4$	$O_6^*C_3H_4BNa$
$O_4Rh^*C_{26}H_{30}N_4$	$O_6^*C_6BF_4Mn$
$O_4Ru^*C_4H_2$	$O_6^*C_6Cr$
$O_4S^*C_3H_8$	$O_6^*C_6H_6B_2Fe_2$
O_4S^*Cu	$O_6^*C_6H_{13}ClMoN_3$
$O_4S^*D_2$	$O_6^*C_{15}H_{21}Co$
$O_4S^*H_2$	$O_6^*C_{15}H_{21}Mo$
$O_4S^*H_3N$	$O_6^*C_{16}H_{10}Cr_2$
$O_4Si^*C_8H_{20}$	$O_6^*Cl_6H_{12}IrNa_2$
$O_4Si^*C_{11}H_{26}$	$O_6Os^*Cl_6H_{12}Na_2$
$O_4Si^*C_{22}H_{16}Fe$	$O_6P^*C_2H_{16}Co$
$O_4Sn^*C_8H_{20}$	$O_6PS^*C_{18}H_{13}ClN$
$O_4V^*C_9H_5$	$O_6PW_2^*C_{16}H_{11}F_6$
$O_5^*C_4H_{10}BLi$	$O_6P_2^*C_4H_{13}N$
$O_5^*C_5Fe$	$O_6P_2^*C_8H_{21}N$
$O_5^*C_5HMn$	$O_6P_2^*C_{10}H_2F_{12}Fe_2$
$O_5^*C_7H_7AsCr$	$O_6P_2^*C_{10}H_{24}$
$O_5^*C_7H_7AsMo$	$O_6P_2^*C_{12}H_{29}N$
$O_5^*C_7H_7CrP$	$O_6P_2^*K_4N_2$
$O_5^*C_7H_7MoP$	$O_6P_3Pt_6^*C_{58}H_{47}F_6$
$O_5^*C_9H_6AsCrF_6P$	O_6P_4
$O_5^*C_9H_6AsF_6MoO_3P$	P_4O_6
$O_5^*C_9H_6As_2CrF_6$	Hydrolysis to H_3PO_3 : 1.5.3.2.1
$O_5^*C_9H_6As_2F_6Mo$	$O_6P_4Ru_3^*C_{56}H_{46}$
$O_5^*C_{14}H_{15}N$	$O_6Ru_3^*C_{44}H_{36}As_4$
$O_5^*C_{14}H_{17}N$	$O_6S^*C_2H_4N_2$
$O_5^*C_{23}H_{45}FeN_5$	$O_6S_2^*H_3N$
$O_5Os^*C_5$	$O_6V^*C_6H$
$O_5P^*C_7HCrF_6$	$O_6W^*C_6$
$O_5P^*C_7HF_6Mo$	$O_6W_2^*C_{16}H_{10}$
$O_5PN^*C_{22}H_{17}Mn$	$O_7^*CoH_2N_2$
$O_5PO_5^*C_9H_6AsF_6Mo$	$O_7Os_2P_2^*C_{39}H_{31}Cl$
$O_5PV^*C_{23}H_{16}$	$O_7PRE^*C_{26}H_{18}Mo$
$O_5P_2^*C_9H_6CrF_6$	$O_7P_2^*C_{37}H_{30}BrIr$
$O_5P_2^*C_9H_6F_6Mo$	$O_7P_2^*C_{37}H_{30}ClIr$
$O_5P_2^*C_9H_{12}Cr$	$O_7P_2^*C_{37}H_{30}IIr$
$O_5P_2^*C_9H_{12}Mo$	$O_7P_2^*C_{39}H_{30}ClIr$
$O_5P_2^*C_{23}H_{15}AuMn$	$O_7Ru_3^*C_{57}H_{43}As_4$
$O_5P_2^*C_{23}H_{15}F_6Mn$	$O_8^*C_4H_4AlLi$
$O_5P_3^*C_{53}H_{40}FeIr$	$O_8^*C_6F_3Mn$
$O_5P_3^*C_{53}H_{42}FeIr$	$O_8^*C_8Fe_2Na_2$
$O_5Re^*C_5H$	$O_8^*C_8H_{12}Mo_2$
$O_5Re^*C_5Na$	$O_8Co_2^*C_8$
$O_5Re^*C_6H_4Br$	$O_8Os_2^*C_8H_2$
$O_5Rh^*C_6H_5$	$O_8Os_3^*C_{10}H_6F_3N$
$O_5Ru^*C_{25}H_{16}Cl_2N_4$	$O_8Os_3^*C_{20}H_{14}N_2$
$O_5Ru_2^*C_{17}H_{16}$	$O_8P_2^*C_{44}H_{31}Fe_2N$
$O_5Ti^*C_{13}H_{24}Cl_2Mg_2N$	$O_8P_2S_2^*C_{16}H_{36}Ir_2$
$O_5V^*C_5HNa_2$	$O_8P_2S_2^*C_{16}H_{38}Ir_2$
$O_5V^*C_5Na_3$	$O_8P_4Ru_3^*C_{58}H_{44}$

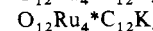
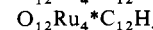
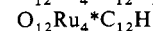
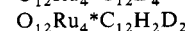
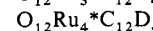
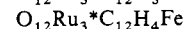
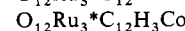
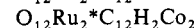
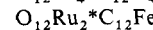
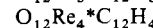
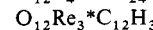
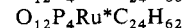
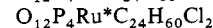
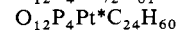
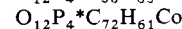
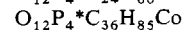
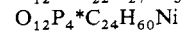
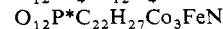
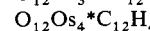
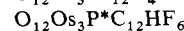
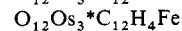
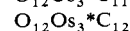
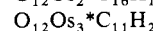
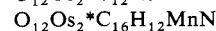
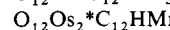
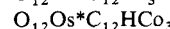
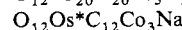
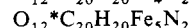
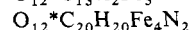
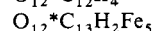
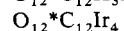
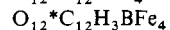
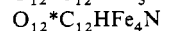
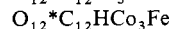
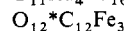
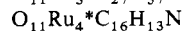
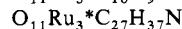
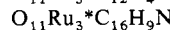
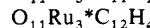
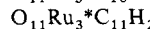
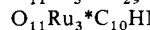
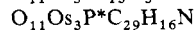
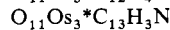
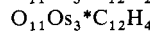
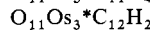
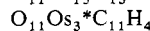
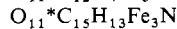
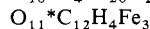
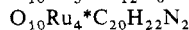
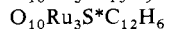
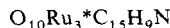
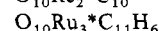
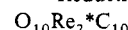


Electrolysis in H_2SO_4 : 1.6.3.4.1



Reaction with H: 1.5.2.2

Reduction by $\text{Li}[\text{AlH}_4]$: 1.5.5.2.2



$O_{13} * C_{18} H_7 Fe_4 N$
 $O_{13} * C_{43} H_{30} Fe_5 N_6$
 $O_{13} Os_3 * C_{13} H_2 Fe$
 $O_{13} Ru_2 * C_{13} Co_2$
 $O_{13} Ru_3 * C_{13} CoK$
 $O_{13} Ru_3 * C_{13} HCo$
 $O_{13} Ru_3 * C_{13} H_2 Fe$
 $O_{13} Ru_4 * C_{13} HK$
 $O_{13} Ru_4 * C_{13} H_2$
 $O_{13} Ru_4 * C_{13} K_2$
 $O_{14} * C_{14} HFe_5 N$
 $O_{14} P * C_{20} H_{22} Co_3 Fe$
 $O_{15} * C_{15} Co_6 K_2$
 $O_{15} * C_{15} HCo_6 K$
 $O_{15} P_5 * C_{15} H_{45} Fe$
 $O_{15} P_6 * C_{15} H_{46} F_6 Fe$
 $O_{16} Re_4 * C_{12} H_4$
 $O_{17} P_2 * H_{25} Na_3$
 $O_{18} Os_6 * C_{18}$
 $O_{18} Os_6 * C_{18} H_2$
 $O_{18} P_2 Ru_6 * C_{54} H_{31} N$
 $O_{18} P_4 Ru_6 * C_{90} H_{60} N_2$
 $O_{30} * C_{42} H_{36} Co_7 Fe_2$
 $Os * C_4 H_2 O_4$
 $Os * C_4 Na_2 O_4$
 $Os * C_5 H_4 O_4$
 $Os * C_5 O_3$
 $Os * C_{11} H_{18} O$
 $Os * C_{12} Co_3 NaO_{12}$
 $Os * C_{12} HCo_3 O_{12}$
 $Os * C_{12} H_{16} O_2$
 $Os * Cl_6 H_{12} Na_2 O_6$
 $Os * O_4$
 $OsP * C_{25} H_{16} ClF_6 N_4 O$
 $OsP * C_{25} H_{17} F_6 N_4 O$
 $OsP_2 * C_{36} H_{30} N_2 O_2$
 $OsP_2 * C_{36} H_{32} Cl_2 N_2 O_2$
 $OsP_2 * C_{37} H_{30} ClNO_2$
 $OsP_2 * C_{37} H_{31} Cl_2 NO_2$
 $OsP_2 * C_{39} H_{30} O_3$
 $OsP_3 * C_{30} H_{43} Cl_2$
 $OsP_3 * C_{42} H_{72} Cl_3$
 $OsP_3 * C_{54} H_{49}$
 $OsP_3 * C_{55} H_{46} ClO$
 $OsP_3 * C_{55} H_{47} O$
 $OsP_3 * C_{56} H_{45} O_2$
 $OsP_4 * C_{12} H_{38}$
 $OsP_4 * F_{12} H_2$
 $Os_2 * C_8 H_2 O_8$
 $Os_2 * C_{12} HMnO_{12}$
 $Os_2 * C_{16} H_{12} MnNO_{12}$
 $Os_2 * C_{22} H_{30} O_2$

$Os_2 * C_{22} H_{32} O_2$
 $Os_2 P_2 * C_{39} H_{31} ClO_7$
 $Os_3 * C_{10} HIO_{10}$
 $Os_3 * C_{10} H_2 O_{10}$
 $Os_3 * C_{10} H_6 F_3 NO_8$
 $Os_3 * C_{11} H_2 O_{12}$
 $Os_3 * C_{11} H_4 F_3 NO_9$
 $Os_3 * C_{11} H_4 O_9$
 $Os_3 * C_{11} H_4 O_{11}$
 $Os_3 * C_{11} H_6 O_{10}$
 $Os_3 * C_{12} H_2 F_3 NO_{10}$
 $Os_3 * C_{12} H_2 O_{11}$
 $Os_3 * C_{12} H_4 F_3 NO_{10}$
 $Os_3 * C_{12} H_4 FeO_{12}$
 $Os_3 * C_{12} H_4 O_{11}$
 $Os_3 * C_{12} H_{12}$
 $Os_3 * C_{12} O_{12}$
 $Os_3 * C_{13} H_2 FeO_{13}$
 $Os_3 * C_{13} H_3 NO_{11}$
 $Os_3 * C_{14} H_6 N_2 O_{10}$
 $Os_3 * C_{15} H_7 NO_9$
 $Os_3 * C_{16} H_7 NO_{10}$
 $Os_3 * C_{17} H_{12} NO_9$
 $Os_3 * C_{20} H_{14} N_2 O_8$
 $Os_3 * C_{26} H_{28} O_{10}$
 $Os_3 P * C_{12} HF_6 O_{12}$
 $Os_3 P * C_{29} H_{16} NO_{11}$
 $Os_3 PS * C_{21} H_{21} O_9$
 $Os_3 P_2 S * C_{21} H_{22} F_6 O_9$
 $Os_3 S * C_9 H_2 O_9$
 $Os_3 S * C_{12} H_6 O_{10}$
 $Os_3 Si_3 * C_9 H_3 Cl_9 O_9$
 $Os_4 * C_{12} H_4 O_{12}$
 $Os_6 * C_{18} H_2 O_{18}$
 $Os_6 * C_{18} O_{18}$

P

Reaction with $NaClO_2$ to form Na_2^*
 $[H_2P_2O_4]$: 1.5.6.2

P_{red}

Reaction with CsH: 1.5.4.2.1

P*Al

P*AsH₄

P*BrF₂

P*BrH₄

P*Br₂F

P*Br₃

P*Br₃O

P*CCl₂F₃

P*CF₃I₂

P*CF₅

P*CH

P*CHF₇K

$P^*CH_2F_3$
 $P^*CH_2F_3O_2$
 $P^*CH_3Cl_2$
 $P^*CH_4F_3$
 $P^*CH_4O_2$
 P^*CH_5
 $P^*CH_5O_2$
 P^*CH_7Ge
 $P^*C_2F_6I$
 $P^*C_2F_7$
 $P^*C_2HCl_7N$
 $P^*C_2HF_6$
 $P^*C_2HF_9K$
 $P^*C_2H_2Cl_7FN$
 $P^*C_2H_5Cl_2$
 $P^*C_2H_6Cl$
 $P^*C_2H_6ClO_2$
 $P^*C_2H_6D$
 $P^*C_2H_6F_2N$
 $P^*C_2H_6F_3$
 $P^*C_2H_7$
 $P^*C_2H_7O$
 $P^*C_2H_7O_2$
 $P^*C_2H_7O_3$
 $P^*C_2H_8B$
 $P^*C_2H_8Cl$
 $P^*C_2H_9F_5N$
 $P^*C_2H_9Ge$
 $P^*C_2H_{10}B$
 $P^*C_3F_9$
 $P^*C_3H_5F_2$
 $P^*C_3H_6F_3$
 $P^*C_3H_6N$
 $P^*C_3H_7Cl_2$
 $P^*C_3H_9O_2$
 $P^*C_3H_9O_3$
 $P^*C_4H_9Cl_2$
 $P^*C_4H_{10}F_3$
 $P^*C_4H_{10}Li$
 $P^*C_4H_{11}$
 $P^*C_4H_{11}O_2$
 $P^*C_4H_{11}O_3$
 $P^*C_4H_{12}ClN_2$
 $P^*C_4H_{12}N$
 $P^*C_5H_{10}ClO$
 $P^*C_5H_{10}F_2O$
 $P^*C_5H_{11}$
 $P^*C_5H_{11}O$
 $P^*C_5H_{11}O_2$
 $P^*C_5H_{13}O_3$
 $P^*C_5H_{15}N_2$
 $P^*C_6H_4F_7N_2$

$P^*C_6H_5Cl_2$
 $P^*C_6H_5Cl_2O$
 $P^*C_6H_5D_2$
 $P^*C_6H_5F_2$
 $P^*C_6H_5F_6N_2$
 $P^*C_6H_5Na_2$
 $P^*C_6H_6FO$
 $P^*C_6H_7$
 $P^*C_6H_7O_2$
 $P^*C_6H_7O_3$
 $P^*C_6H_8N$
 $P^*C_6H_9MoNO_4$
 $P^*C_6H_9O_3$
 $P^*C_6H_{12}NO_3$
 $P^*C_6H_{13}$
 $P^*C_6H_{13}BF_4NO_3$
 $P^*C_6H_{15}O_2$
 $P^*C_6H_{15}O_3$
 $P^*C_6H_{16}N$
 $P^*C_6H_{18}N_3$
 $P^*C_7HCrF_6O_5$
 $P^*C_7HF_6MoO_5$
 $P^*C_7H_7Cl_2$
 $P^*C_7H_7F_6N_2$
 $P^*C_7H_9$
 $P^*C_7H_9F_2O$
 $P^*C_7H_9O$
 $P^*C_7H_9O_2$
 $P^*C_7H_{17}O_3$
 $P^*C_8H_5F_6MoO_3$
 $P^*C_8H_8F_5O$
 $P^*C_8H_9$
 $P^*C_8H_{10}NO$
 $P^*C_8H_{10}NO_3$
 $P^*C_8H_{11}$
 $P^*C_8H_{11}F_2O$
 $P^*C_8H_{11}N_2O$
 $P^*C_8H_{11}O_2$
 $P^*C_8H_{11}O_3$
 $P^*C_8H_{17}N_4$
 $P^*C_8H_{18}ClO$
 $P^*C_8H_{19}$
 $P^*C_8H_{19}O_2$
 $P^*C_8H_{19}O_3$
 $P^*C_8H_{20}N$
 $P^*C_9H_7F_8O$
 $P^*C_9H_{19}N_4$
 $P^*C_9H_{21}Ge$
 $P^*C_9H_{21}O_3$
 $P^*C_9H_{22}ClGe$
 $P^*C_9H_{23}Ge$
 $P^*C_{10}H_{10}ClO$

$P^*C_{10}H_{11}$
 $P^*C_{10}H_{13}N_2O$
 $P^*C_{10}H_{14}ClO$
 $P^*C_{10}H_{14}NO_2$
 $P^*C_{10}H_{14}NO_3$
 $P^*C_{10}H_{15}O$
 $P^*C_{10}H_{15}O_3$
 $P^*C_{10}H_{16}NO_2$
 $P^*C_{10}H_{25}Ge$
 $P^*C_{11}H_{14}NO_3$
 $P^*C_{11}H_{16}NO$
 $P^*C_{11}H_{17}N$
 $P^*C_{11}H_{17}O_3$
 $P^*C_{12}HF_6O_{12}Os_3$
 $P^*C_{12}H_{10}Cl$
 $P^*C_{12}H_{10}ClO$
 $P^*C_{12}H_{10}Cl_3$
 $P^*C_{12}H_{10}D$
 $P^*C_{12}H_{10}Li$
 $P^*C_{12}H_{10}Na$
 $P^*C_{12}H_{11}$
 $P^*C_{12}H_{11}O$
 $P^*C_{12}H_{11}O_2$
 $P^*C_{12}H_{11}O_3$
 $P^*C_{12}H_{15}O_3$
 $P^*C_{12}H_{15}O_4$
 $P^*C_{12}H_{16}NO_3$
 $P^*C_{12}H_{18}NO_3$
 $P^*C_{12}H_{23}$
 $P^*C_{12}H_{23}O_2$
 $P^*C_{12}H_{23}O_3$
 $P^*C_{12}H_{25}N_4$
 $P^*C_{12}H_{27}O_3$
 $P^*C_{12}H_{28}N$
 $P^*C_{12}H_{30}N_3$
 $P^*C_{13}H_6Co_3F_6O_9$
 $P^*C_{13}H_{10}Cl$
 $P^*C_{13}H_{11}Cl_2$
 $P^*C_{13}H_{13}O_2$
 $P^*C_{13}H_{15}N_3$
 $P^*C_{13}H_{26}Ir$
 $P^*C_{14}H_{10}ClD_2Fe_2O_4$
 $P^*C_{14}H_{11}F_6Fe_2O_4$
 $P^*C_{14}H_{12}ClFe_2O_4$
 $P^*C_{14}H_{12}F_5O$
 $P^*C_{14}H_{13}$
 $P^*C_{14}H_{13}O_2$
 $P^*C_{14}H_{14}ClO$
 $P^*C_{14}H_{15}$
 $P^*C_{14}H_{15}BCl_3O$
 $P^*C_{14}H_{15}O_2$
 $P^*C_{14}H_{16}NO$
 $P^*C_{14}H_{16}NO_2$
 $P^*C_{14}H_{29}O$
 $P^*C_{14}H_{30}O$
 $P^*C_{15}H_{16}MnO_2$
 $P^*C_{16}H_{20}N$
 $P^*C_{17}H_{20}N$
 $P^*C_{18}H_{15}$
 $P^*C_{18}H_{15}BrN$
 $P^*C_{18}H_{15}O_2$
 $P^*C_{18}H_{15}O_3$
 $P^*C_{18}H_{16}Cu$
 $P^*C_{18}H_{16}N$
 $P^*C_{18}H_{17}BrN$
 $P^*C_{18}H_{17}ClN$
 $P^*C_{18}H_{18}B$
 $P^*C_{18}H_{18}N_3$
 $P^*C_{18}H_{20}LiO_2$
 $P^*C_{18}H_{21}O_2$
 $P^*C_{18}H_{22}Nb$
 $P^*C_{18}H_{23}B_3Cu$
 $P^*C_{18}H_{25}Ge$
 $P^*C_{19}H_{15}ClIrO$
 $P^*C_{19}H_{15}O$
 $P^*C_{19}H_{17}$
 $P^*C_{19}H_{18}Cl$
 $P^*C_{19}H_{18}N$
 $P^*C_{20}H_{20}N$
 $P^*C_{20}H_{22}Co_3FeO_{14}$
 $P^*C_{20}H_{42}CoN_4O_4$
 $P^*C_{21}H_{16}CoO_3$
 $P^*C_{21}H_{16}CoO_6$
 $P^*C_{21}H_{20}BrNi$
 $P^*C_{22}H_{16}MnO_4$
 $P^*C_{22}H_{27}Co_3FeNO_{12}$
 $P^*C_{23}H_{21}Ni$
 $P^*C_{24}H_{17}$
 $P^*C_{24}H_{20}N$
 $P^*C_{25}H_{16}ClF_6N_4OOs$
 $P^*C_{25}H_{17}F_6N_4OOs$
 $P^*C_{25}H_{20}ClFeO_2$
 $P^*C_{25}H_{20}ReO_2$
 $P^*C_{25}H_{21}FeO_3$
 $P^*C_{25}H_{22}MnO$
 $P^*C_{25}H_{23}MnO$
 $P^*C_{26}H_{21}CrO_2$
 $P^*C_{26}H_{41}FeO_2$
 $P^*C_{26}H_{42}BF_4FeO_2$
 $P^*C_{27}H_{26}ClMo$
 $P^*C_{28}H_{21}IrNO_2$
 $P^*C_{28}H_{22}ClIrNO_2$
 $P^*C_{28}H_{32}B_{10}IrO_2$
 $P^*C_{29}H_{16}NO_{11}Os_3$

- $P^*C_{29}H_{30}B_{10}IrO_3$
 $P^*C_{29}H_{32}B_{10}IrO_3$
 $P^*C_{29}H_{33}B_{10}IrNO$
 $P^*C_{29}H_{35}B_{10}IrNO$
 $P^*C_{34}H_{35}B_{10}IrNO$
 $P^*C_{34}H_{37}B_{10}IrNO$
 $P^*C_{36}H_{30}AuGe$
 $P^*C_{36}H_{31}AuGe$
 P^*ClF_2
 P^*ClH_4
 P^*Cl_2F
 P^*Cl_3
 P^*Cl_3O
 $P^*CsF_4H_2$
 P^*CsH_2
 P^*D
 P^*D_2H
 P^*D_3
 $P^*D_3O_3$
 P^*F_2H
 $P^*F_2H_2N$
 $P^*F_2H_3$
 $P^*F_2H_5N_2$
 P^*F_2I
 P^*F_3
 $P^*F_3H_2$
 P^*F_5
 P^*F_5H
 P^*F_5HK
 P^*F_6H
 P^*Ga
 P^*GeH_5
 $P^*Ge_2H_7$
 $P^*Ge_3H_9$
 P^*H
 P^*H_2K
 P^*H_2Li
 $P^*H_2NaO_2$
 P^*H_3
 $P^*H_3O_2$
 $P^*H_3O_3$
 $P^*H_3O_4$
 P^*H_4I
 $P^*H_6N_3O$
 P^*I_3
 P^*In
 $PN^*C_{22}H_{17}MnO_5$
 $PO_5^*C_7H_7Cr$
 $PO_5^*C_7H_7Mo$
 $PO_5^*C_9H_6AsCrF_6$
 $PO_5^*C_9H_6AsF_6MoO_5$
 $PPt^*C_{15}H_{33}$
 $PPt^*C_{16}H_{27}$
 $PPt^*C_{16}H_{35}$
 $PPt^*C_{17}H_{38}BF_4O$
 $PPt^*C_{18}H_{31}$
 $PPt^*C_{25}H_{20}Cl_2N$
 $PPt^*C_{27}H_{26}Cl_2NO$
 $PPTs_2^*C_{21}H_{23}$
 $PPTs_3^*C_{24}H_{29}$
 $Pre^*C_7H_5F_6NO_3$
 $Pre^*C_{23}H_{21}NO$
 $Pre^*C_{24}H_{21}NO_3$
 $Pre^*C_{25}H_{20}O_2$
 $Pre^*C_{26}H_{18}MoO_7$
 $PRh^*C_{11}H_{14}F_6$
 $PRh^*C_{14}H_{28}$
 $PRh^*C_{26}H_{30}N_4O_4$
 $PRhSi^*C_{36}H_{31}Cl$
 $PRh_2^*C_{20}H_{33}F_6O_3$
 $PRh_3^*C_{30}H_{48}F_6O$
 $PRu^*C_{21}H_{17}F_6N_4O$
 $PRu^*C_{30}H_{35}$
 $PS^*C_2H_7$
 $PS^*C_4H_{11}$
 $PS^*C_8H_{19}$
 $PS^*C_{10}H_{17}N_2$
 $PS^*C_{12}H_8Cl_2NO_4$
 $PS^*C_{12}H_{13}N_2$
 $PS^*C_{14}H_{15}BCl_3$
 $PS^*C_{14}H_{16}NO$
 $PS^*C_{18}H_{13}ClNO_6$
 $PS^*C_{21}H_{21}O_9Os_3$
 $PSSi^*C_5H_{16}N$
 $PSSi^*C_{11}H_{27}N$
 $PSSi^*C_{12}H_{31}N_2O$
 $PSSi_2^*C_8H_{24}N$
 $PSSi_2^*C_{10}H_{27}N_2$
 $PSSi_2^*C_{11}H_{31}N_2O$
 $PS_2^*C_4H_{11}O_2$
 $PS_2Si^*C_{12}H_{29}O_2$
 $PS_3^*C_2H_9N$
 $PS_3^*HNa_2$
 $PSi^*C_3H_7$
 $PSi^*C_2H_7D_2$
 $PSi^*C_5H_{15}$
 $PSi^*C_5H_{18}B$
 $PSi^*C_9H_{15}$
 $PSi^*C_{11}H_{27}O$
 $PSi^*C_{16}H_{28}O_4$
 $PSi^*C_{26}H_{33}N$
 PSi^*H_4Li
 PSi^*H_5
 $PSi_2^*C_2H_{11}$

$\text{PSi}_2^*\text{C}_6\text{H}_{18}\text{F}_2\text{N}$
 $\text{PSi}_2^*\text{C}_6\text{H}_{19}$
 $\text{PSi}_2^*\text{C}_6\text{H}_{20}\text{N}$
 $\text{PSi}_2^*\text{C}_{10}\text{H}_{27}\text{N}_2$
 $\text{PSi}_2^*\text{C}_{11}\text{H}_{23}\text{Ni}$
 $\text{PSi}_2^*\text{C}_{12}\text{H}_{23}$
 $\text{PSi}_2^*\text{H}_6\text{Li}$
 PSi_2^*H_7
 $\text{PSi}_3^*\text{C}_9\text{H}_{27}\text{N}$
 $\text{PSi}_3^*\text{C}_9\text{H}_{27}\text{N}_2$
 $\text{PSi}_3^*\text{C}_9\text{H}_{29}\text{N}_2$
 PSi_3^*H_9
 $\text{PSi}_4^*\text{C}_{10}\text{H}_{46}\text{N}_3$
 $\text{PSi}_5^*\text{C}_{15}\text{H}_{46}\text{N}_3$
 $\text{PSn}^*\text{C}_{10}\text{H}_{17}$
 $\text{PSn}^*\text{C}_{12}\text{H}_{21}\text{O}_2$
 $\text{PSn}^*\text{C}_{15}\text{H}_{27}\text{O}_2$
 $\text{PSn}^*\text{C}_{18}\text{H}_{25}$
 $\text{PSn}^*\text{C}_{30}\text{H}_{25}$
 $\text{PV}^*\text{C}_{23}\text{H}_{16}\text{O}_5$
 $\text{PW}^*\text{C}_{10}\text{H}_{15}\text{O}_2$
 $\text{PW}^*\text{C}_{11}\text{H}_{11}\text{F}_7\text{N}_2$
 $\text{PW}^*\text{C}_{11}\text{H}_{12}\text{F}_6\text{N}_2$
 $\text{PW}^*\text{C}_{12}\text{H}_{15}\text{F}_6\text{N}_2$
 $\text{PW}_2^*\text{C}_{16}\text{H}_{11}\text{F}_6\text{O}_6$
 P_2^*Al_3
 $\text{P}_2^*\text{As}_2\text{Ca}_6$
 $\text{P}_2^*\text{BaD}_4\text{O}_4$
 $\text{P}_2^*\text{BaH}_2\text{O}_4$
 $\text{P}_2^*\text{BaH}_4\text{O}_4$
 $\text{P}_2^*\text{CH}_3\text{F}_3$
 $\text{P}_2^*\text{CH}_4\text{AsF}_3$
 P_2^*CH_6
 $\text{P}_2^*\text{CH}_8\text{Ge}$
 $\text{P}_2^*\text{C}_2\text{Cl}_6\text{N}_2$
 $\text{P}_2^*\text{C}_2\text{F}_6$
 $\text{P}_2^*\text{C}_2\text{H}_2\text{F}_6$
 $\text{P}_2^*\text{C}_2\text{H}_8$
 $\text{P}_2^*\text{C}_3\text{H}_{10}\text{Ge}$
 $\text{P}_2^*\text{C}_3\text{H}_{10}$
 $\text{P}_2^*\text{C}_4\text{H}_6\text{F}_6$
 $\text{P}_2^*\text{C}_4\text{H}_{12}$
 $\text{P}_2^*\text{C}_4\text{H}_{13}\text{NO}_6$
 $\text{P}_2^*\text{C}_4\text{H}_{14}\text{Ge}$
 $\text{P}_2^*\text{C}_4\text{H}_{18}\text{B}_2$
 $\text{P}_2^*\text{C}_6\text{H}_{23}\text{Ir}$
 $\text{P}_2^*\text{C}_7\text{H}_{10}$
 $\text{P}_2^*\text{C}_7\text{H}_{18}\text{ClIrO}$
 $\text{P}_2^*\text{C}_8\text{H}_{18}\text{K}_2$
 $\text{P}_2^*\text{C}_8\text{H}_{21}\text{NO}_6$
 $\text{P}_2^*\text{C}_9\text{H}_6\text{CrF}_6\text{O}_5$
 $\text{P}_2^*\text{C}_9\text{H}_6\text{F}_6\text{MoO}_5$
 $\text{P}_2^*\text{C}_9\text{H}_{12}\text{CrO}_5$
 $\text{P}_2^*\text{C}_9\text{H}_{12}\text{MoO}_5$
 $\text{P}_2^*\text{C}_9\text{H}_{22}$
 $\text{P}_2^*\text{C}_{10}\text{H}_2\text{F}_{12}\text{Fe}_2\text{O}_6$
 $\text{P}_2^*\text{C}_{10}\text{H}_{12}\text{Mo}$
 $\text{P}_2^*\text{C}_{10}\text{H}_{24}\text{O}_6$
 $\text{P}_2^*\text{C}_{11}\text{H}_{18}\text{O}_3$
 $\text{P}_2^*\text{C}_{11}\text{H}_{23}\text{Co}$
 $\text{P}_2^*\text{C}_{12}\text{H}_{12}$
 $\text{P}_2^*\text{C}_{12}\text{H}_{29}\text{NO}_6$
 $\text{P}_2^*\text{C}_{13}\text{H}_{30}\text{ClIrO}$
 $\text{P}_2^*\text{C}_{14}\text{H}_{16}$
 $\text{P}_2^*\text{C}_{14}\text{H}_{22}\text{Co}_2$
 $\text{P}_2^*\text{C}_{14}\text{H}_{24}$
 $\text{P}_2^*\text{C}_{16}\text{H}_{33}\text{Co}$
 $\text{P}_2^*\text{C}_{18}\text{H}_{24}\text{O}_3$
 $\text{P}_2^*\text{C}_{19}\text{H}_{42}\text{BrIrO}$
 $\text{P}_2^*\text{C}_{19}\text{H}_{42}\text{ClIrO}$
 $\text{P}_2^*\text{C}_{19}\text{H}_{42}\text{IrO}$
 $\text{P}_2^*\text{C}_{21}\text{H}_{46}\text{BrIr}$
 $\text{P}_2^*\text{C}_{21}\text{H}_{46}\text{ClIr}$
 $\text{P}_2^*\text{C}_{21}\text{H}_{49}\text{Ir}$
 $\text{P}_2^*\text{C}_{22}\text{H}_{48}\text{ClIr}$
 $\text{P}_2^*\text{C}_{22}\text{H}_{51}\text{Ir}$
 $\text{P}_2^*\text{C}_{23}\text{H}_{15}\text{AuMnO}_5$
 $\text{P}_2^*\text{C}_{23}\text{H}_{15}\text{F}_6\text{MnO}_5$
 $\text{P}_2^*\text{C}_{24}\text{H}_{20}$
 $\text{P}_2^*\text{C}_{24}\text{H}_{22}\text{N}_4$
 $\text{P}_2^*\text{C}_{24}\text{H}_{23}\text{N}_3$
 $\text{P}_2^*\text{C}_{26}\text{H}_{22}\text{Mn}_2\text{O}_4$
 $\text{P}_2^*\text{C}_{26}\text{H}_{26}\text{BCuO}_2$
 $\text{P}_2^*\text{C}_{26}\text{H}_{26}\text{Cl}_4\text{Mo}$
 $\text{P}_2^*\text{C}_{26}\text{H}_{28}\text{BCu}$
 $\text{P}_2^*\text{C}_{26}\text{H}_{30}\text{ClIr}$
 $\text{P}_2^*\text{C}_{27}\text{H}_{24}\text{D}_3\text{IrO}$
 $\text{P}_2^*\text{C}_{27}\text{H}_{25}\text{IrO}$
 $\text{P}_2^*\text{C}_{27}\text{H}_{27}\text{IrO}$
 $\text{P}_2^*\text{C}_{29}\text{H}_{37}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{29}\text{H}_{39}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{30}\text{H}_{39}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{30}\text{H}_{41}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{33}\text{H}_{38}\text{ClIrO}$
 $\text{P}_2^*\text{C}_{35}\text{H}_{39}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{35}\text{H}_{41}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{35}\text{H}_{43}\text{B}_{10}\text{IrO}$
 $\text{P}_2^*\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_2\text{Os}$
 $\text{P}_2^*\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{N}_2\text{O}_2\text{Os}$
 $\text{P}_2^*\text{C}_{36}\text{H}_{33}\text{Cl}_3\text{IrNO}$
 $\text{P}_2^*\text{C}_{36}\text{H}_{34}\text{BCu}$
 $\text{P}_2^*\text{C}_{36}\text{H}_{35}\text{Ir}$
 $\text{P}_2^*\text{C}_{36}\text{H}_{36}\text{BF}_4\text{IrO}_2$
 $\text{P}_2^*\text{C}_{36}\text{H}_{38}\text{AgB}_3$

- $P_2^*C_{36}H_{38}B_3Cu$
 $P_2^*C_{36}H_{38}B_5Cu$
 $P_2^*C_{36}H_{39}B_6Cu$
 $P_2^*C_{36}H_{66}Cl_2Ni$
 $P_2^*C_{36}H_{66}Ni$
 $P_2^*C_{36}H_{67}ClNi$
 $P_2^*C_{37}H_{30}BrIrO$
 $P_2^*C_{37}H_{30}BrIrO_7$
 $P_2^*C_{37}H_{30}ClIr$
 $P_2^*C_{37}H_{30}ClIrO$
 $P_2^*C_{37}H_{30}ClIrO_7$
 $P_2^*C_{37}H_{30}ClNO_2Os$
 $P_2^*C_{37}H_{30}IIrO$
 $P_2^*C_{37}H_{30}IIrO_7$
 $P_2^*C_{37}H_{31}ClIrN$
 $P_2^*C_{37}H_{31}Cl_2IrO$
 $P_2^*C_{37}H_{31}Cl_2NO_2Os$
 $P_2^*C_{37}H_{31}D_2IrO$
 $P_2^*C_{37}H_{31}IrO$
 $P_2^*C_{37}H_{32}ClIrO$
 $P_2^*C_{37}H_{33}IrO$
 $P_2^*C_{37}H_{38}B_3IrO$
 $P_2^*C_{37}H_{66}BrIrO$
 $P_2^*C_{37}H_{66}ClIrO$
 $P_2^*C_{37}H_{66}IIrO$
 $P_2^*C_{38}H_{31}IrO_2$
 $P_2^*C_{38}H_{34}OPtS$
 $P_2^*C_{38}H_{36}B_2CuN_2$
 $P_2^*C_{38}H_{40}BF_4IrO_2$
 $P_2^*C_{39}H_{30}ClIrO_7$
 $P_2^*C_{39}H_{30}O_3Os$
 $P_2^*C_{39}H_{31}ClO_7Os_2$
 $P_2^*C_{39}H_{41}B_{10}IrO$
 $P_2^*C_{39}H_{43}B_{10}IrO$
 $P_2^*C_{40}H_{31}FeNO_4$
 $P_2^*C_{40}H_{33}IrO_4$
 $P_2^*C_{40}H_{38}BF_4IrN_2$
 $P_2^*C_{40}H_{43}B_{10}IrO$
 $P_2^*C_{40}H_{44}BF_4IrO_2$
 $P_2^*C_{40}H_{45}B_{10}IrO$
 $P_2^*C_{40}H_{58}Fe$
 $P_2^*C_{40}H_{71}NNi$
 $P_2^*C_{42}H_{38}Mo$
 $P_2^*C_{42}H_{44}BF_4IrO_2$
 $P_2^*C_{42}H_{48}BF_4IrO_2$
 $P_2^*C_{42}H_{72}NiO$
 $P_2^*C_{43}H_{36}Fe$
 $P_2^*C_{43}H_{37}ClFe$
 $P_2^*C_{43}H_{42}ClIrO$
 $P_2^*C_{44}H_{31}Fe_2NO_8$
 $P_2^*C_{44}H_{42}BF_4Ir$
 $P_2^*C_{44}H_{43}Ir$
 $P_2^*C_{44}H_{48}BF_4IrO_2$
 $P_2^*C_{44}H_{52}BF_4IrO_2$
 $P_2^*C_{45}H_{45}B_{10}IrO$
 $P_2^*C_{45}H_{47}B_{10}IrO$
 $P_2^*Ca_3$
 $P_2^*Cl_4H_2N_2O_2$
 $P_2^*Cl_5NO$
 $P_2^*D_4$
 $P_2^*Ge_5H_{14}$
 $P_2^*H_2Na_2O_4$
 $P_2^*H_4$
 $P_2^*H_{25}Na_3O_{17}$
 $P_2^*I_4$
 $P_2IrS^*C_{36}H_{32}Cl$
 $P_2^*K_4N_2O_6$
 $P_2^*Mg_3$
 $P_2^*Na_4$
 $P_2Pd^*C_{20}H_{43}F_3O_2$
 $P_2Pd^*C_{24}H_{54}$
 $P_2Pd^*C_{28}H_{46}$
 $P_2Pd^*C_{48}H_{60}Ge$
 $P_2Pd^*C_{48}H_{60}Ge_2$
 $P_2Pt^*CH_{44}Cl_2Ge$
 $P_2Pt^*C_6H_{20}$
 $P_2Pt^*C_8H_{22}$
 $P_2Pt^*C_{12}H_{30}$
 $P_2Pt^*C_{12}H_{30}Cl_2$
 $P_2Pt^*C_{12}H_{31}Br$
 $P_2Pt^*C_{12}H_{31}Cl$
 $P_2Pt^*C_{12}H_{31}I$
 $P_2Pt^*C_{12}H_{32}$
 $P_2Pt^*C_{13}H_{30}BClF_4O$
 $P_2Pt^*C_{13}H_{31}ClO_2$
 $P_2Pt^*C_{14}H_{34}$
 $P_2Pt^*C_{14}H_{35}Cl$
 $P_2Pt^*C_{15}H_{37}Cl$
 $P_2Pt^*C_{18}H_{35}ClN_2$
 $P_2Pt^*C_{18}H_{36}$
 $P_2Pt^*C_{18}H_{36}ClN$
 $P_2Pt^*C_{18}H_{36}Cl_2N_2$
 $P_2Pt^*C_{18}H_{42}$
 $P_2Pt^*C_{18}H_{44}$
 $P_2Pt^*C_{18}H_{44}O$
 $P_2Pt^*C_{19}H_{36}ClNO$
 $P_2Pt^*C_{19}H_{39}BF_4O$
 $P_2Pt^*C_{19}H_{44}$
 $P_2Pt^*C_{22}H_{26}BF_4O$
 $P_2Pt^*C_{22}H_{34}$
 $P_2Pt^*C_{24}H_{54}$
 $P_2Pt^*C_{27}H_{28}$
 $P_2Pt^*C_{27}H_{44}$

$P_2Pt^*C_{28}H_{46}$
 $P_2Pt^*C_{28}H_{47}Cl$
 $P_2Pt^*C_{33}H_{54}Ge_2$
 $P_2Pt^*C_{34}H_{52}$
 $P_2Pt^*C_{36}H_{30}N_6$
 $P_2Pt^*C_{36}H_{31}Cl$
 $P_2Pt^*C_{36}H_{66}$
 $P_2Pt^*C_{36}H_{68}$
 $P_2Pt^*C_{37}H_{31}N$
 $P_2Pt^*C_{39}H_{31}F_6N$
 $P_2Pt^*C_{42}H_{36}ClN$
 $P_2Pt^*C_{42}H_{67}F_5$
 $P_2Pt^*C_{43}H_{36}ClNO$
 $P_2Pt^*C_{48}H_{60}Ge_2$
 $P_2Pt^*C_{50}H_{40}$
 $P_2Pt^*C_{54}H_{72}Ge_2$
 $P_2PtS^*C_{36}H_{32}$
 $P_2PtSn^*C_{27}H_{58}$
 $P_2PtSn^*C_{42}H_{48}$
 $P_2Pt_2Si_2^*C_{40}H_{80}$
 $P_2Pt_2Si_2^*C_{52}H_{90}$
 $P_2Re^*C_{12}H_{23}Cl_3N$
 $P_2Re^*C_{12}H_{30}N$
 $P_2Re^*C_{16}H_{29}$
 $P_2Re^*C_{20}H_{30}Cl_3O$
 $P_2Re^*C_{20}H_{37}$
 $P_2Re^*C_{26}H_{33}$
 $P_2Re^*C_{36}H_{37}$
 $P_2Re^*C_{42}H_{43}$
 $P_2Re^*C_{43}H_{37}Cl_3N$
 $P_2Re^*C_{43}H_{38}Cl_2N$
 $P_2Rh^*C_8H_{19}$
 $P_2Rh^*C_{18}H_{43}$
 $P_2Rh^*C_{18}H_{45}$
 $P_2Rh^*C_{19}H_{45}O_3$
 $P_2Rh^*C_{21}H_{44}Cl$
 $P_2Rh^*C_{21}H_{46}Cl$
 $P_2Rh^*C_{24}H_{55}N_2$
 $P_2Rh^*C_{24}H_{57}$
 $P_2Rh^*C_{37}H_{30}ClO$
 $P_2Rh^*C_{40}H_{37}O$
 $P_2Rh^*C_{46}H_{49}ClN_2$
 $P_2Rh^*C_{46}H_{51}ClN_2$
 $P_2Rh^*C_{47}H_{47}ClN$
 $P_2Rh^*C_{47}H_{49}ClN$
 $P_2RhS^*C_{36}H_{32}Cl$
 $P_2RhS^*C_{46}H_{50}Cl$
 $P_2RhS^*C_{46}H_{52}Cl$
 $P_2Ru^*C_{16}H_{33}Cl$
 $P_2Ru^*C_{16}H_{34}$
 $P_2Ru^*C_{30}H_{36}F_6$
 $P_2Ru^*C_{36}H_{34}O_2$

$P_2Ru^*C_{36}H_{72}$
 $P_2Ru^*C_{38}H_{32}O_2$
 $P_2Ru^*C_{41}H_{35}Cl$
 $P_2Ru^*C_{41}H_{36}$
 $P_2RuSi^*C_{20}H_{44}$
 $P_2Ru_6^*C_{54}H_{31}NO_{18}$
 $P_2S^*C_{21}H_{22}F_6O_9Os_3$
 $P_2S_2^*C_4H_{12}$
 $P_2S_2^*C_6H_{20}$
 $P_2S_2^*C_{16}H_{36}$
 $P_2S_2^*C_{16}H_{36}Ir_2N_6O_2$
 $P_2S_2^*C_{16}H_{36}Ir_2O_2$
 $P_2S_2^*C_{16}H_{36}Ir_2O_8$
 $P_2S_2^*C_{16}H_{38}Ir_2N_6O_2$
 $P_2S_2^*C_{16}H_{38}Ir_2O_2$
 $P_2S_2^*C_{16}H_{38}Ir_2O_8$
 $P_2S_2^*C_{24}H_{22}N_2$
 $P_2S_2^*C_{46}H_{48}Ir_2O_2$
 $P_2S_2^*C_{46}H_{50}Ir_2O_2$
 $P_2Si_4^*C_{22}H_{46}Ni_2$
 $P_2Ta^*C_6H_{21}$
 $P_2V^*C_{43}H_{39}BNO_2$
 $P_2W^*C_{16}H_{22}Cl_4$
 $P_2W^*C_{28}H_{30}Cl_4$
 $P_2W^*C_{52}H_{48}N_4$
 P_2Zn_3
 Zn_3P_2
 Reaction with aq acid: 1.5.3.2.1
 $P_3^*CH_4Cl_4N_3$
 $P_3^*CH_4F_3$
 $P_3^*C_2H_6Cl_4N_3$
 $P_3^*C_3H_2F_9$
 $P_3^*C_3H_8Cl_4N_3$
 $P_3^*C_6H_{21}N_6$
 $P_3^*C_6H_{24}B_3$
 $P_3^*C_8H_{12}CrF_9$
 $P_3^*C_8H_{18}K$
 $P_3^*C_8H_{19}$
 $P_3^*C_9H_{28}Cl_4Ir$
 $P_3^*C_{11}H_{24}CoF_6$
 $P_3^*C_{12}H_{21}MoO_3$
 $P_3^*C_{12}H_{51}B_{30}ClIr$
 $P_3^*C_{14}H_{23}Co_2F_6$
 $P_3^*C_{14}H_{32}B_2CoF_8$
 $P_3^*C_{15}H_{15}D_6Ni_3$
 $P_3^*C_{15}H_{21}Ni_3$
 $P_3^*C_{16}H_{34}CoF_6$
 $P_3^*C_{18}H_{45}Cl_3Ir$
 $P_3^*C_{18}H_{46}Cl_2Ir$
 $P_3^*C_{24}H_{35}Br_2MoN_2$
 $P_3^*C_{24}H_{37}BCu$
 $P_3^*C_{24}H_{51}Mo$

$P_3^*C_{25}H_{23}DN_3$
 $P_3^*C_{25}H_{24}AuClN_3$
 $P_3^*C_{25}H_{24}N_3$
 $P_3^*C_{28}H_{28}MoN_4$
 $P_3^*C_{30}H_{43}Cl_2Os$
 $P_3^*C_{31}H_{32}N$
 $P_3^*C_{36}H_{37}ClIr$
 $P_3^*C_{36}H_{39}ClIr$
 $P_3^*C_{39}H_{30}F_6IrO_3$
 $P_3^*C_{39}H_{41}B_{10}IrO$
 $P_3^*C_{42}H_{32}F_{12}IrN_4$
 $P_3^*C_{42}H_{47}AgBO_2$
 $P_3^*C_{42}H_{72}Cl_3Os$
 $P_3^*C_{52}H_{40}FeIrO_4$
 $P_3^*C_{52}H_{44}FeIrO_4$
 $P_3^*C_{53}H_{40}FeIrO_5$
 $P_3^*C_{53}H_{42}FeIrO_5$
 $P_3^*C_{54}H_{45}ClCu$
 $P_3^*C_{54}H_{45}ClIr$
 $P_3^*C_{54}H_{45}IrNO$
 $P_3^*C_{54}H_{46}CoN_2$
 $P_3^*C_{54}H_{48}Co$
 $P_3^*C_{54}H_{48}Ir$
 $P_3^*C_{54}H_{49}Os$
 $P_3^*C_{54}H_{51}Cu_6$
 $P_3^*C_{54}H_{53}AgB_3$
 $P_3^*C_{55}H_{46}ClOOS$
 $P_3^*C_{55}H_{46}IrO$
 $P_3^*C_{55}H_{47}OOS$
 $P_3^*C_{55}H_{48}BCuN$
 $P_3^*C_{56}H_{45}O_2Os$
 $P_3^*C_{56}H_{51}AgBO_2$
 $P_3^*C_{56}H_{51}BCuO_2$
 $P_3^*C_{66}H_{55}DGeNi$
 $P_3^*C_{66}H_{56}GeNi$
 $P_3^*Cl_6N_3$
 $P_3^*H_5$
 $P_3Ir^*C_{34}H_{38}F_6$
 $P_3Pd^*C_{27}H_{63}$
 $P_3Pd^*C_{42}H_{66}B$
 $P_3Pt^*C_{18}H_{45}$
 $P_3Pt^*C_{27}H_{63}$
 $P_3Pt^*C_{42}H_{37}O_2$
 $P_3Pt^*C_{54}H_{45}$
 $P_3Pt_3^*C_{36}H_{87}$
 $P_3Pt_6^*C_{58}H_{47}F_6O_6$
 $P_3Re^*C_{24}H_{33}Cl_3$
 $P_3Re^*C_{24}H_{38}$
 $P_3Re^*C_{30}H_{45}Cl_3$
 $P_3Re^*C_{30}H_{50}$
 $P_3Re^*C_{39}H_{44}$
 $P_3Re^*C_{54}H_{50}$

$P_3Rh^*C_{26}H_{64}$
 $P_3Rh^*C_{27}H_{64}$
 $P_3Rh^*C_{42}H_{45}Cl_2$
 $P_3Rh^*C_{54}H_{45}Cl$
 $P_3Rh^*C_{54}H_{46}$
 $P_3Rh^*C_{54}H_{47}Cl$
 $P_3Rh^*C_{55}H_{46}O$
 $P_3Rh^*C_{63}H_{63}Cl$
 $P_3Rh^*C_{63}H_{65}Cl$
 $P_3Ru^*C_{31}H_{46}ClO$
 $P_3Ru^*C_{54}H_{45}Cl_2$
 $P_3Ru^*C_{54}H_{46}Cl$
 $P_3Ru^*C_{54}H_{46}NO$
 $P_3Ru^*C_{54}H_{47}N_2$
 $P_3Ru^*C_{55}H_{47}O$
 $P_3Ru^*C_{56}H_{49}O_2$
 $P_3Si^*C_{11}H_{27}$
 $P_3Si^*C_{12}H_{31}$
 $P_3Si_4^*C_{12}H_{36}Cl$
 $P_3W^*C_9H_{27}Cl_4$
 $P_3W^*C_9H_{33}$
 $P_3W^*C_{24}H_{33}Cl_4$
 $P_3W^*C_{24}H_{35}Br_2N_2$
 $P_3W^*C_{24}H_{36}Br_2ClN_2$
 $P_3W^*C_{24}H_{39}$
 $P_3W^*C_{27}H_{39}Br_2N_2$
P₄

Deuterolysis with D_2O : 1.5.7.1.2

Disproportionation in $Ba(OH)_2$ soln:
1.5.3.2.1

Hydrolysis to form $[H_2PO_2]^-$: 1.5.6.2

Hydrolysis to form $[HPO_3]^{2-}$: 1.5.6.2

Hydrolysis to form PH_3 : 1.5.6.2

Reaction with $(h^5-C_5H_5)_2MoH_2$:
1.5.4.2.2

Reaction with alkenes and O_2 : 1.5.4.2.2

Reaction with $(CH_3)_4Sn_2$: 1.5.4.2.2

Reaction with CH_3NH_2 over carbon to
form CH_3PH_2 : 1.5.6.2

Reaction with NH_3 : 1.5.4.2.2

Reaction with N_2H_4 : 1.5.4.2.2

Reaction with $[n-BuO]^-/n-BuOH$:
1.5.3.2.2

Reaction with CH_4 : 1.5.4.2.2

Reaction with C_2H_4 : 1.5.4.2.2

Reaction with C_3H_8 : 1.5.4.2.2

Reaction with HI : 1.5.3.2.3

Reaction with aq base: 1.5.3.2.1

Reaction with olefins and O_2 : 1.5.6.2

P₄ C_4F_{12}

P₄ $C_4H_{12}K_2$

P₄ $C_4H_{12}Li_2$

- $P_4^*C_8H_{20}K_2$
 $P_4^*C_8H_{20}Li_2$
 $P_4^*C_{12}H_{36}Fe$
 $P_4^*C_{12}H_{36}Ge_6$
 $P_4^*C_{12}H_{38}Os$
 $P_4^*C_{13}H_{32}ClIrO$
 $P_4^*C_{20}H_{48}Cl_2Fe$
 $P_4^*C_{20}H_{49}ClRh$
 $P_4^*C_{24}H_{22}$
 $P_4^*C_{24}H_{44}K_2$
 $P_4^*C_{24}H_{44}Li_2$
 $P_4^*C_{24}H_{52}F_6Mo$
 $P_4^*C_{24}H_{60}Ge_6$
 $P_4^*C_{24}H_{60}NiO_{12}$
 $P_4^*C_{32}H_{44}MoN_4$
 $P_4^*C_{32}H_{45}Co$
 $P_4^*C_{36}H_{85}CoO_{12}$
 $P_4^*C_{52}H_{48}Cl_2Fe$
 $P_4^*C_{52}H_{48}MoN_4$
 $P_4^*C_{52}H_{49}Br_2MoN$
 $P_4^*C_{52}H_{49}ClFe$
 $P_4^*C_{52}H_{50}Br_2MoN_2$
 $P_4^*C_{52}H_{50}Fe$
 $P_4^*C_{52}H_{52}Mo$
 $P_4^*C_{52}H_{52}MoN_4$
 $P_4^*C_{52}H_{56}Mo$
 $P_4^*C_{53}H_{51}IMoN_2$
 $P_4^*C_{53}H_{52}BF_4IMoN_2$
 $P_4^*C_{54}H_{48}ClIr$
 $P_4^*C_{56}H_{57}BrMoN_2$
 $P_4^*C_{57}H_{56}MoO_2$
 $P_4^*C_{57}H_{58}MoN_2$
 $P_4^*C_{60}H_{64}MoN_4$
 $P_4^*C_{60}H_{68}Mo$
 $P_4^*C_{64}H_{82}BIr$
 $P_4^*C_{72}H_{61}CoO_{12}$
 $P_4^*C_{72}H_{64}B_2Cu_2F_4$
 $P_4^*C_{72}H_{70}B_{10}Cu_2$
 $P_4^*C_{84}H_{84}Cl_2Rh_2$
 $P_4^*CoF_{12}H$
 $P_4^*F_{12}FeH_2$
 $P_4^*F_{12}H_2Os$
 $P_4^*O_6$
 $P_4^*O_{10}$
 $P_4Pd^*C_{12}H_{36}$
 $P_4Pd^*C_{24}H_{60}$
 $P_4Pd^*C_{52}H_{52}$
 $P_4Pt^*C_{24}H_{60}O_{12}$
 $P_4Pt^*C_{72}H_{60}$
 $P_4Pt_2^*C_{38}H_{84}$
 $P_4Pt_2^*C_{50}H_{44}Cl_2$
 $P_4Pt_2^*C_{50}H_{47}$
 $P_4Pt_2^*C_{51}H_{45}O$
 $P_4Pt_2^*C_{52}H_{44}O_2$
 $P_4Pt_2S^*C_{51}H_{49}F_6$
 $P_4Pt_4^*C_{48}H_{84}$
 $P_4Re^*C_{32}H_{47}$
 $P_4Re^*C_{52}H_{55}$
 $P_4Re^*C_{72}H_{63}$
 $P_4Rh^*C_{26}H_{24}F_6$
 $P_4Rh^*C_{54}H_{52}BF_4$
 $P_4Rh^*C_{54}H_{54}BF_4$
 $P_4Rh^*C_{62}H_{64}BF_4O_4$
 $P_4Rh^*C_{62}H_{66}BF_4O_4$
 $P_4Rh^*C_{72}H_{61}$
 $P_4Rh^*F_{12}H$
 $P_4Rh^*F_{12}K$
 $P_4Ru^*C_{13}H_{39}Cl$
 $P_4Ru^*C_{13}H_{40}$
 $P_4Ru^*C_{24}H_{60}Cl_2O_{12}$
 $P_4Ru^*C_{24}H_{62}O_{12}$
 $P_4Ru^*C_{52}H_{50}$
 $P_4Ru^*C_{52}H_{54}$
 $P_4Ru^*C_{54}H_{54}$
 $P_4Ru^*C_{56}H_{58}$
 $P_4Ru^*F_{12}H_2$
 $P_4Ru_2^*C_{36}H_{88}$
 $P_4Ru_3^*C_{56}H_{46}O_6$
 $P_4Ru_3^*C_{58}H_{44}O_8$
 $P_4Ru_6^*C_{90}H_{60}N_2O_{18}$
 $P_4S^*C_{52}H_{51}MoN_2O_4$
 $P_4Si_2^*C_{30}H_{38}$
 $P_4Si_4^*C_{12}H_{36}$
 $P_4Ta^*C_{12}H_{32}Cl_2$
 $P_4Ta_2^*C_{12}H_{38}Cl_6$
 $P_4W^*C_{32}H_{44}N_4$
 $P_4W^*C_{52}H_{48}N_4$
 $P_4W^*C_{52}H_{50}Br_2N_2$
 $P_4W^*C_{52}H_{51}BrN_2$
 $P_4W^*C_{52}H_{52}N_4$
 $P_4W^*C_{52}H_{56}$
 $P_4W^*C_{53}H_{52}BrClN_2$
 $P_4W^*C_{76}H_{64}$
 $P_5^*C_{12}H_{36}F_6Ir$
 $P_5^*C_{13}H_{38}F_6IrO$
 $P_5^*C_{15}H_{45}FeO_{15}$
 $P_5^*C_{24}H_{53}F_{12}Mo$
 $P_5^*C_{30}H_{25}$
 $P_5^*H_4Li$
 $P_5^*H_5$
 $P_5Pt_2^*C_{50}H_{45}Cl_2F_6$
 $P_5Pt_2^*C_{51}H_{45}F_6O$
 $P_5Pt_2^*C_{54}H_{54}ClF_6$
 $P_5Pt_2^*C_{54}H_{55}F_6$

$\text{P}_5\text{Re}^*\text{F}_{15}\text{H}$
 $\text{P}_5\text{W}^*\text{C}_{52}\text{H}_{57}\text{F}_6$
 $\text{P}_6^*\text{C}_{15}\text{H}_{46}\text{F}_6\text{FeO}_{15}$
 $\text{P}_6^*\text{C}_{18}\text{H}_{58}\text{Mo}_2$
 $\text{P}_6\text{Ru}_2^*\text{C}_{18}\text{H}_{56}\text{O}$
 $\text{P}_6\text{Ru}_2^*\text{C}_{21}\text{H}_{60}$
 $\text{P}_6\text{Ru}_2^*\text{C}_{60}\text{H}_{90}\text{Cl}_4$
 $\text{P}_6\text{Ru}_3^*\text{C}_{75}\text{H}_{68}$
 P_7^*HLi_2
 $\text{P}_8\text{Ta}_2^*\text{C}_{36}\text{H}_{96}\text{Al}_2\text{O}_8$
Pb

Electrochemical reduction to PbH_4 :

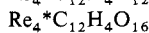
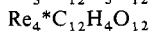
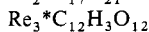
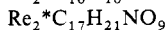
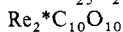
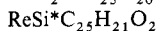
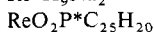
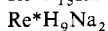
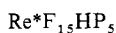
1.6.3.5

Reaction with atomic hydrogen: 1.6.2.5

$\text{Pb}^*\text{C}_2\text{H}_6\text{Cl}_2$
 $\text{Pb}^*\text{C}_2\text{H}_8$
 $\text{Pb}^*\text{C}_3\text{H}_9\text{Cl}$
 $\text{Pb}^*\text{C}_3\text{H}_{10}$
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 $\text{Pb}^*\text{C}_6\text{H}_{15}\text{Li}$
 $\text{Pb}^*\text{C}_6\text{H}_{16}$
 $\text{Pb}^*\text{C}_6\text{H}_{19}\text{B}$
 $\text{Pb}^*\text{C}_7\text{H}_{18}$
 $\text{Pb}^*\text{C}_7\text{H}_{19}\text{N}$
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 $\text{Pb}^*\text{C}_{18}\text{H}_{34}$
 Pb^*Cl_2
 Pb^*H_4
 Pb^*Mg_2
 Pb_2^*H_2
 Pd^*Ag
 $\text{Pd}^*\text{C}_{12}\text{H}_{36}\text{P}_4$
 $\text{Pd}^*\text{C}_{20}\text{H}_{43}\text{F}_3\text{O}_2\text{P}_2$

$\text{Pd}^*\text{C}_{24}\text{H}_{54}\text{P}_2$
 $\text{Pd}^*\text{C}_{24}\text{H}_{60}\text{P}_4$
 $\text{Pd}^*\text{C}_{27}\text{H}_{63}\text{P}_3$
 $\text{Pd}^*\text{C}_{28}\text{H}_{46}\text{P}_2$
 $\text{Pd}^*\text{C}_{42}\text{H}_{66}\text{BP}_3$
 $\text{Pd}^*\text{C}_{48}\text{H}_{60}\text{GeP}_2$
 $\text{Pd}^*\text{C}_{48}\text{H}_{60}\text{Ge}_2\text{P}_2$
 $\text{Pd}^*\text{C}_{52}\text{H}_{52}\text{P}_4$
 Pd^*Cu
 Pd^*H
 $\text{Pd}^*\text{La}_2\text{O}_3$
 PdZr_2^*O
 $\text{Pd}_2^*\text{C}_{56}\text{H}_{40}\text{Cl}_4$
 $\text{Pi}_4^*\text{C}_{52}\text{H}_{48}\text{Ni}$
 Pr^*Co_2
 Pr^*Co_5
 Pr^*H_2
 Pr^*Ni_2
 Pr^*Ni_5
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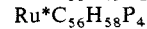
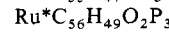
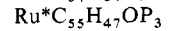
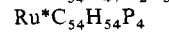
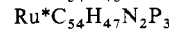
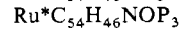
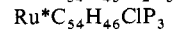
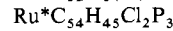
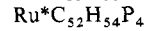
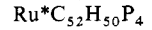
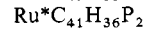
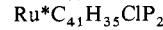
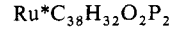
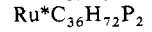
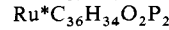
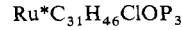
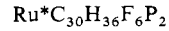
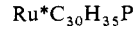
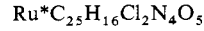
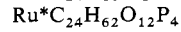
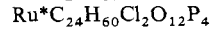
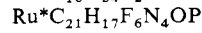
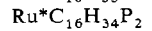
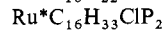
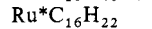
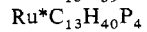
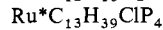
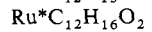
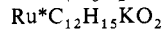
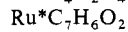
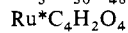
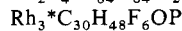
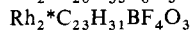
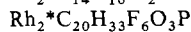
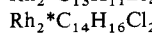
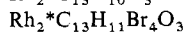
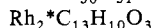
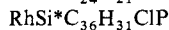
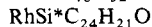
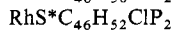
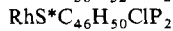
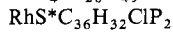
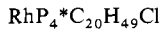
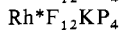
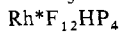
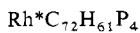
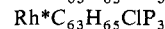
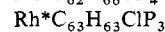
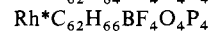
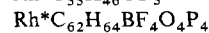
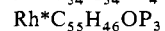
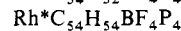
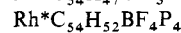
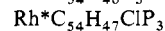
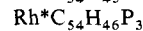
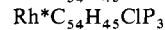
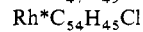
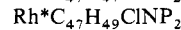
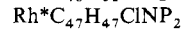
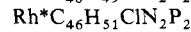
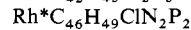
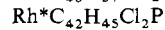
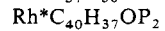
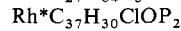
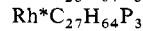
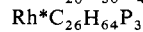
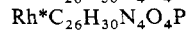
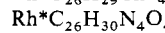
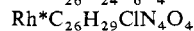
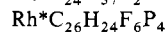
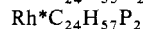
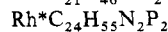
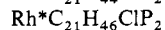
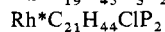
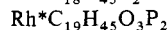
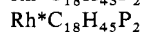
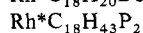
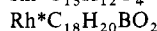
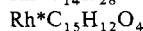
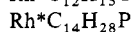
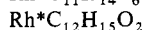
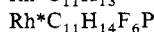
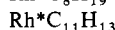
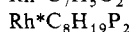
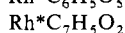
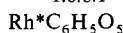
- Pt*C₂₄H₅₄P₂
 Pt*C₂₄H₅₅As₂Cl
 Pt*C₂₄H₅₆As₂
 Pt*C₂₄H₆₀O₁₂P₄
 Pt*C₂₅H₂₀Cl₂NP
 Pt*C₂₆H₅₅As₂F₃O₂
 Pt*C₂₇H₂₆Cl₂NOP
 Pt*C₂₇H₂₈P₂
 Pt*C₂₇H₄₄P₂
 Pt*C₂₇H₆₃P₃
 Pt*C₂₈H₄₆P₂
 Pt*C₂₈H₄₇ClP₂
 Pt*C₃₃H₅₄Ge₂P₂
 Pt*C₃₄H₅₂P₂
 Pt*C₃₆H₃₀N₆P₂
 Pt*C₃₆H₃₁ClP₂
 Pt*C₃₆H₆₆P₂
 Pt*C₃₆H₆₈P₂
 Pt*C₃₇H₃₁NP₂
 Pt*C₃₉H₃₁F₆NP₂
 Pt*C₄₂H₃₆CINP₂
 Pt*C₄₂H₃₇O₂P₃
 Pt*C₄₂H₆₇F₅P₂
 Pt*C₄₃H₃₆CINOP₂
 Pt*C₄₆H₆₀Ge₂P₂
 Pt*C₅₀H₄₀P₂
 Pt*C₅₄H₄₅P₃
 Pt*C₅₄H₇₂Ge₂P₂
 Pt*C₇₂H₆₀P₄
 Pt*Cl₆H₂
 PtS*C₃₆H₃₂P₂
 PtSP₂*C₃₈H₃₄O
 PtS₂*C₂₁H₂₃P
 PtS₃*C₂₄H₂₉P
 PtSn*C₂₇H₅₈P₂
 PtSn₂*C₄₂H₄₈P₂
 Pt₂*C₃₂H₃₀F₈O₂
 Pt₂*C₃₂H₃₁BF₁₂O₂
 Pt₂*C₃₈H₈₄P₄
 Pt₂*C₅₀H₄₄Cl₂P₄
 Pt₂*C₅₀H₄₅Cl₂F₆P₅
 Pt₂*C₅₀H₄₇P₄
 Pt₂*C₅₁H₄₅F₆OP₅
 Pt₂*C₅₁H₄₅OP₄
 Pt₂*C₅₂H₄₄O₂P₄
 Pt₂*C₅₄H₅₄ClF₆P₅
 Pt₂*C₅₄H₅₅F₆P₅
 Pt₂S*C₅₁H₄₉F₆P₄
 Pt₂Si₂*C₄₀H₈₀P₂
 Pt₂Si₂*C₅₂H₉₀P₂
 Pt₃*C₃₆H₈₇P₃
 Pt₄*C₄₈H₈₄P₄
- Pt₅*La
 Pt₆*C₅₈H₄₇F₆O₆P₃
Ra
 Reaction with H₂: 1.8.3
 Rb*H
 Rb*H₂N
 Rb₂*C₂
 Re*C₅HO₅
 Re*C₅NaO₅
 Re*C₆H₄BrO₅
 Re*C₆H₆NO₂
 Re*C₇H₃F₆NO₃P
 Re*C₇H₆NO₃
 Re*C₇H₆NO₄
 Re*C₇H₇O₂
 Re*C₇H₈NO₂
 Re*C₇H₈NO₃
 Re*C₈H₅O₃
 Re*C₉H₉O₃
 Re*C₁₀H₁₁
 Re*C₁₀H₁₂Cl
 Re*C₁₂H₂₃Cl₃NP₂
 Re*C₁₂H₃₀NP₂
 Re*C₁₄H₉BF₇N₂O₂
 Re*C₁₄H₁₀F₃N₂O₂
 Re*C₁₄H₁₂BF₄N₂O₂
 Re*C₁₄H₁₃N₂O₂
 Re*C₁₅H₁₅N₂O₂
 Re*C₁₅H₁₆BF₄N₂O₂
 Re*C₁₅H₁₉O₃
 Re*C₁₆H₂₉P₂
 Re*C₂₀H₃₀Cl₃OP₂
 Re*C₂₀H₃₇P₂
 Re*C₂₃H₂₁NOP
 Re*C₂₄H₂₁NO₃P
 Re*C₂₄H₃₃Cl₃P₃
 Re*C₂₄H₃₈P₃
 Re*C₂₅H₂₀O₂P
 Re*C₂₆H₁₈MoO₇P
 Re*C₂₆H₃₃P₂
 Re*C₃₀H₄₅Cl₃P₃
 Re*C₃₀H₅₀P₃
 Re*C₃₂H₄₇P₄
 Re*C₃₆H₃₇P₂
 Re*C₃₉H₄₄P₃
 Re*C₄₂H₄₃P₂
 Re*C₄₃H₃₇Cl₃NP₂
 Re*C₄₃H₃₈Cl₂NP₂
 Re*C₅₂H₅₅P₄
 Re*C₅₄H₅₀P₃
 Re*C₇₂H₆₃P₄
 Re*Cl₅



Rh

Catalysis of CO reaction with H_2 :

1.6.6.1



Ru*Cl₃
 Ru*Cl₃NO
 Ru*F₁₂H₂P₄
 RuSi*C₂₀H₄₄P₂
 Ru₂*C₁₂FeO₁₂
 Ru₂*C₁₂H₂Co₂O₁₂
 Ru₂*C₁₃Co₂O₁₃
 Ru₂*C₁₄H₁₂O₃
 Ru₂*C₁₅H₁₄O₃
 Ru₂*C₁₅H₁₆O₂
 Ru₂*C₁₆H₁₄O₃
 Ru₂*C₁₆H₁₅BF₄O₃
 Ru₂*C₁₇H₁₆O₅
 Ru₂*C₁₈H₅₆OP₆
 Ru₂*C₂₁H₆₀P₆
 Ru₂*C₃₆H₈₈P₄
 Ru₂*C₆₀H₉₀Cl₄P₆
 Ru₂*Ce
 Ru₂*Dy
 Ru₂*Er
 Ru₂*Gd
 Ru₂*Ho
 Ru₂*La
 Ru₂*Nd
 Ru₃*C₁₀HNO₁₁
 Ru₃*C₁₁H₂O₁₁
 Ru₃*C₁₁H₆O₁₀
 Ru₃*C₁₂H₃CoO₁₂
 Ru₃*C₁₂H₄FeO₁₂
 Ru₃*C₁₂H₄O₁₁
 Ru₃*C₁₂O₁₂
 Ru₃*C₁₃CoKO₁₃
 Ru₃*C₁₃HCoO₁₃
 Ru₃*C₁₃H₂FeO₁₃
 Ru₃*C₁₄H₈NiO₉
 Ru₃*C₁₄H₁₁NO₉
 Ru₃*C₁₅H₉NO₁₀
 Ru₃*C₁₅H₁₀O₉
 Ru₃*C₁₆H₉NO₁₁
 Ru₃*C₁₈H₁₈O₃
 Ru₃*C₁₈H₂₀N₂O₈
 Ru₃*C₂₇H₃₇NO₁₁
 Ru₃*C₄₄H₃₆As₄O₆
 Ru₃*C₅₆H₄₆O₆P₄
 Ru₃*C₅₇H₄₃As₄O₇
 Ru₃*C₅₈H₄₄As₄O₈
 Ru₃*C₅₈H₄₄O₈P₄
 Ru₃*C₇₅H₆₈P₆
 Ru₃S*C₁₂H₆O₁₀
 Ru₄*C₁₂D₄O₁₂
 Ru₄*C₁₂H₂D₂O₁₂
 Ru₄*C₁₂H₃BO₁₂
 Ru₄*C₁₂H₄O₁₂
 Ru₄*C₁₂K₄O₁₂
 Ru₄*C₁₃HKO₁₃
 Ru₄*C₁₃H₂O₁₃
 Ru₄*C₁₃K₂O₁₃
 Ru₄*C₁₆H₁₃NO₁₁
 Ru₄*C₂₀H₂₂N₂O₁₀
 Ru₆*C₅₄H₃₁NO₁₈P₂
 Ru₆*C₉₀H₆₀N₂O₁₈P₄
 S*C₂H₄N₂O₆
 S*C₂H₆Ge
 S*C₂H₇P
 S*C₃H₅N
 S*C₃H₈O₄
 S*C₄H₁₁P
 S*C₈H₁₉P
 S*C₉H₂O₉Os₃
 S*C₁₀H₁₇N₂P
 S*C₁₂H₆O₁₀Os₃
 S*C₁₂H₆O₁₀Ru₃
 S*C₁₂H₈Cl₂NO₄P
 S*C₁₂H₁₃N₂P
 S*C₁₄H₁₅BCl₃P
 S*C₁₄H₁₆NOP
 S*C₁₈H₁₃CINO₆P
 S*C₂₁H₂₁O₉Os₃P
 S*C₂₁H₂₂F₆O₉Os₃P₂
 S*C₃₆H₃₂CIP₂Ir
 S*C₃₆H₃₂CIP₂Rh
 S*C₃₆H₃₂P₂Pt
 S*C₄₆H₅₀CIP₂Rh
 S*C₄₆H₅₂CIP₂Rh
 S*C₅₁H₄₉F₆P₄Pt₂
 S*C₅₂H₅₁MoN₂O₄P₄
 S*C_uO₄
 S*D₂O₄
 S*H₂
 S*H₂O₄
 S*H₃NO₃
 S*H₃NO₄
 S*H₄N₂O₂
 SO₄*H₂
 SP₂*C₃₈H₃₄OPt
 SSi*C₃H₁₆NP
 SSi*C₉H₂₁N
 SSi*C₁₁H₂₇NP
 SSi*C₁₂H₃₁N₂OP
 SSi₂*C₈H₂₄NP
 SSi₂*C₁₀H₂₇N₂P
 SSi₂*C₁₁H₃₁N₂OP
 STa₆*H₂
 S₂*C₄H₁₁O₂P

$S_2^*C_4H_{12}Ge_2$
 $S_2^*C_4H_{12}P_2$
 $S_2^*C_8H_{20}P_2$
 $S_2^*C_{16}H_{36}Ir_2N_6O_2P_2$
 $S_2^*C_{16}H_{36}Ir_2O_2P_2$
 $S_2^*C_{16}H_{36}Ir_2O_8P_2$
 $S_2^*C_{16}H_{36}P_2$
 $S_2^*C_{16}H_{38}Ir_2N_6O_2P_2$
 $S_2^*C_{16}H_{38}Ir_2O_2P_2$
 $S_2^*C_{16}H_{38}Ir_2O_8P_2$
 $S_2^*C_{21}H_{23}PPt$
 $S_2^*C_{24}H_{22}N_2P_2$
 $S_2^*C_{46}H_{48}Ir_2O_2P_2$
 $S_2^*C_{46}H_{50}Ir_2O_2P_2$
 $S_2^*H_3NO_6$
 $S_2Si^*C_{12}H_{29}O_2P$
 $S_2Sn^*O_8$
 $S_3^*C_2H_9NP$
 $S_3^*C_{24}H_{29}PPt$
 $S_3^*C_{27}H_{16}F_9IrN_4O_9$
 $S_3^*HNa_2P$
 $S_6^*B_3H_3$
 $S_8^*H_5Nb_{21}$

Sb

Cathode in reduction to SbH_3 : 1.5.3.4

Reaction with hydrogen: 1.5.2.4

$Sb^*CH_3Cl_2$
 Sb^*CH_5
 $Sb^*C_2H_5Cl_2$
 $Sb^*C_2H_6Br$
 $Sb^*C_2H_6Cl$
 $Sb^*C_2H_6Li$
 $Sb^*C_2H_7$
 $Sb^*C_3F_9$
 $Sb^*C_4H_9Cl_2$
 $Sb^*C_4H_{10}Br$
 $Sb^*C_4H_{10}Li$
 $Sb^*C_4H_{11}$
 $Sb^*C_6H_5I_2$
 $Sb^*C_6H_7$
 $Sb^*C_6H_9Cl_5N$
 $Sb^*C_6H_{15}$
 $Sb^*C_8H_{18}Cl$
 $Sb^*C_8H_{19}$
 $Sb^*C_{10}H_{19}$
 $Sb^*C_{12}H_{10}Cl$
 $Sb^*C_{12}H_{10}Li$
 $Sb^*C_{12}H_{11}$
 $Sb^*C_{12}H_{22}Cl$
 $Sb^*C_{12}H_{23}$
 $Sb^*C_{18}H_{45}Ge_3$
 Sb^*Cl_3

Sb^*Cl_5
 Sb^*D_3
 $Sb^*Ge_3H_9$
 Sb^*H_3
 Sb^*K_3
 $SbSi_3^*H_9$
 $SbSn_3^*C_9H_{27}$
 $Sb_2^*C_{45}H_{36}Fe_3O_8$
 $Sb_2^*Mg_3$
 $Sb_2^*O_3$
 Sc^*Cl_3
 Sc^*Co_2
 Sc^*Fe_2
 Sc^*H_2
 Sc^*Ni_2
 Se^*Mn_2
 Se^*O_2
Si

Reaction with SiH_4 : 1.6.2.2

Reaction with CH_3Cl and H_2 : 1.6.2.2

Reaction with HCl at high T: 1.6.6.2

$Si^*AsF_3H_2$
 Si^*AsH_4K
 Si^*AsH_5
 $Si^*CH_3Cl_3$
 $Si^*CH_4Cl_2$
 Si^*CH_4O
 Si^*CH_6
 Si^*CH_7As
 $Si^*C_2H_4Cl_4$
 $Si^*C_2H_5Cl_3$
 $Si^*C_2H_6$
 $Si^*C_2H_6AsF_3$
 $Si^*C_2H_6Cl_2$
 $Si^*C_2H_6Cl_2O$
 $Si^*C_2H_6D_2$
 $Si^*C_2H_7$
 $Si^*C_2H_7Cl$
 $Si^*C_2H_7ClO_2$
 $Si^*C_2H_7D_2P$
 $Si^*C_2H_7P$
 $Si^*C_2H_8$
 $Si^*C_2H_8O$
 $Si^*C_2H_8O_2$
 $Si^*C_3H_5$
 $Si^*C_3H_5Cl_3$
 $Si^*C_3H_8$
 $Si^*C_3H_9Cl$
 $Si^*C_3H_9D_2N$
 $Si^*C_3H_9N_3$
 $Si^*C_3H_{10}$
 $Si^*C_3H_{10}F_2Ge$

Si*C ₃ H ₁₀ O	Si*C ₁₂ H ₃₁ N ₂ OPS
Si*C ₃ H ₁₁ As	Si*C ₁₂ H ₃₁ P ₃
Si*C ₄ H ₁₀ Cl ₂	Si*C ₁₃ H ₃₂ Ge
Si*C ₄ H ₁₀ Cl ₂ O ₂	Si*C ₁₆ H ₂₀ O ₂
Si*C ₄ H ₁₀ F ₂	Si*C ₁₆ H ₂₈ O ₄ P
Si*C ₄ H ₁₀ F ₂ O ₂	Si*C ₁₆ H ₃₂ ClIr
Si*C ₄ H ₁₀ N ₄	Si*C ₁₈ H ₁₅ BrMg
Si*C ₄ H ₁₁ Cl	Si*C ₁₈ H ₁₅ Cl
Si*C ₄ H ₁₁ ClO ₂	Si*C ₁₈ H ₁₅ D
Si*C ₄ H ₁₂	Si*C ₁₈ H ₁₆
Si*C ₄ H ₁₂ CIN	Si*C ₁₈ H ₁₈ AlLi
Si*C ₄ H ₁₂ O	Si*C ₁₈ H ₃₉ Cl
Si*C ₄ H ₁₂ O ₂	Si*C ₁₈ H ₄₀
Si*C ₄ H ₁₃ As	Si*C ₂₀ H ₁₈ ClMnO ₂
Si*C ₅ H ₁₁ Cl ₃	Si*C ₂₀ H ₃₀ Ge
Si*C ₅ H ₁₄	Si*C ₂₀ H ₄₄ P ₂ Ru
Si*C ₅ H ₁₅ As	Si*C ₂₂ H ₁₆ FeO ₄
Si*C ₅ H ₁₅ P	Si*C ₂₄ H ₂₁ ORh
Si*C ₅ H ₁₆ NPS	Si*C ₂₅ H ₂₁ O ₂ Re
Si*C ₅ H ₁₈ BP	Si*C ₂₅ H ₂₂
Si*C ₆ H ₅ Cl ₃	Si*C ₂₅ H ₂₃ MnO ₂
Si*C ₆ H ₈	Si*C ₂₆ H ₃₃ NP
Si*C ₆ H ₁₃ Cl ₃	Si*C ₃₁ H ₂₅ LiO
Si*C ₆ H ₁₅ Cl	Si*C ₃₁ H ₂₆ O
Si*C ₆ H ₁₅ F	Si*C ₃₆ H ₃₁ ClPRh
Si*C ₆ H ₁₆	Si*Ca
Si*C ₆ H ₁₆ O	Si*ClH ₃
Si*C ₆ H ₁₆ O ₂	Si*Cl ₃ H
Si*C ₆ H ₁₇ N	Si*Cl ₄
Si*C ₆ H ₁₈ Ge	Si*Cl ₆ Ge
Si*C ₇ H ₁₆	Si*DH ₃
Si*C ₇ H ₁₉ N	Si*D ₄
Si*C ₈ H ₁₆	Si*F ₂
Si*C ₈ H ₁₈	Si*F ₃ H
Si*C ₈ H ₂₀ O ₂	Si*GeH ₆
Si*C ₈ H ₂₀ O ₄	Si*GeMg ₄
Si*C ₉ H ₁₂ Cl ₂	Si*GeO ₂
Si*C ₉ H ₁₅ As	Si*Ge ₂ H ₈
Si*C ₉ H ₁₅ P	Si*Ge ₃ H ₁₀
Si*C ₉ H ₂₁ D	Si*Ge ₅ H ₁₄
Si*C ₉ H ₂₁ NS	Si*H ₃ K
Si*C ₉ H ₂₂	Si*H ₃ Li
Si*C ₁₁ H ₂₆ O	Si*H ₃ Na
Si*C ₁₁ H ₂₆ O ₄	Si*H ₄
Si*C ₁₁ H ₂₇ NPS	Si*H ₄ LiP
Si*C ₁₁ H ₂₇ OP	Si*H ₅ P
Si*C ₁₁ H ₂₇ P ₃	Si*Mg ₂
Si*C ₁₂ H ₁₀ Cl ₂	Si*NaO ₃
Si*C ₁₂ H ₁₀ D ₂	Si*O
Si*C ₁₂ H ₁₁ Cl	Si*O ₂
Si*C ₁₂ H ₁₂	Si ₂ *Br ₂ F ₄
Si*C ₁₂ H ₂₉ O ₂ PS ₂	Si ₂ *CH ₈

$\text{Si}_2^*\text{C}_2\text{H}_{10}$	$\text{Si}_3^*\text{AsH}_9$
$\text{Si}_2^*\text{C}_2\text{H}_{11}\text{P}$	$\text{Si}_3^*\text{C}_4\text{H}_{16}$
$\text{Si}_2^*\text{C}_3\text{H}_{10}$	$\text{Si}_3^*\text{C}_6\text{H}_{18}\text{Li}_2$
$\text{Si}_2^*\text{C}_3\text{H}_{12}$	$\text{Si}_3^*\text{C}_6\text{H}_{20}$
$\text{Si}_2^*\text{C}_4\text{H}_{12}$	$\text{Si}_3^*\text{C}_9\text{H}_3\text{Cl}_9\text{O}_9\text{Os}_3$
$\text{Si}_2^*\text{C}_4\text{H}_{12}\text{F}_2$	$\text{Si}_3^*\text{C}_9\text{H}_{24}$
$\text{Si}_2^*\text{C}_4\text{H}_{12}\text{Li}_2$	$\text{Si}_3^*\text{C}_9\text{H}_{27}\text{As}$
$\text{Si}_2^*\text{C}_4\text{H}_{14}$	$\text{Si}_3^*\text{C}_9\text{H}_{27}\text{NP}$
$\text{Si}_2^*\text{C}_4\text{H}_{14}\text{O}$	$\text{Si}_3^*\text{C}_9\text{H}_{27}\text{N}_2\text{P}$
$\text{Si}_2^*\text{C}_4\text{H}_{16}$	$\text{Si}_3^*\text{C}_9\text{H}_{29}\text{N}_2\text{P}$
$\text{Si}_2^*\text{C}_5\text{H}_{15}\text{Cl}$	$\text{Si}_3^*\text{C}_{18}\text{H}_{45}\text{Bi}$
$\text{Si}_2^*\text{C}_5\text{H}_{16}$	Si_3^*Cl_8
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{F}_2\text{NP}$	Si_3^*D_8
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{NNa}$	$\text{Si}_3^*\text{GeH}_{10}$
$\text{Si}_2^*\text{C}_6\text{H}_{18}\text{O}$	$\text{Si}_3^*\text{Ge}_2\text{H}_{12}$
$\text{Si}_2^*\text{C}_6\text{H}_{19}\text{As}$	Si_3^*H_8
$\text{Si}_2^*\text{C}_6\text{H}_{19}\text{N}$	$\text{Si}_3^*\text{H}_9\text{N}$
$\text{Si}_2^*\text{C}_6\text{H}_{19}\text{P}$	$\text{Si}_3^*\text{H}_9\text{P}$
$\text{Si}_2^*\text{C}_6\text{H}_{20}\text{Ge}$	$\text{Si}_3^*\text{H}_9\text{Sb}$
$\text{Si}_2^*\text{C}_6\text{H}_{20}\text{NP}$	$\text{Si}_4^*\text{C}_8\text{H}_{24}\text{Li}_2$
$\text{Si}_2^*\text{C}_7\text{H}_{31}\text{B}_{10}\text{N}$	$\text{Si}_4^*\text{C}_8\text{H}_{26}$
$\text{Si}_2^*\text{C}_8\text{H}_{22}$	$\text{Si}_4^*\text{C}_{10}\text{H}_{46}\text{N}_3\text{P}$
$\text{Si}_2^*\text{C}_8\text{H}_{24}\text{NPS}$	$\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{ClP}_3$
$\text{Si}_2^*\text{C}_{10}\text{H}_{27}\text{As}$	$\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{N}_4$
$\text{Si}_2^*\text{C}_{10}\text{H}_{27}\text{N}_2\text{P}$	$\text{Si}_4^*\text{C}_{12}\text{H}_{36}\text{P}_4$
$\text{Si}_2^*\text{C}_{10}\text{H}_{27}\text{N}_2\text{PS}$	$\text{Si}_4^*\text{C}_{22}\text{H}_{46}\text{Ni}_2\text{P}_2$
$\text{Si}_2^*\text{C}_{11}\text{H}_{23}\text{NiP}$	$\text{Si}_4^*\text{C}_{48}\text{H}_{40}$
$\text{Si}_2^*\text{C}_{11}\text{H}_{31}\text{N}_2\text{OPS}$	$\text{Si}_4^*\text{Cl}_{10}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{23}\text{N}$	$\text{Si}_4^*\text{D}_{10}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{23}\text{P}$	$\text{Si}_4^*\text{GeH}_{12}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{28}\text{Cl}_2$	$\text{Si}_4^*\text{H}_{10}$
$\text{Si}_2^*\text{C}_{12}\text{H}_{30}$	$\text{Si}_4\text{Sn}^*\text{C}_{12}\text{H}_{36}\text{N}_2$
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$\text{Si}_2^*\text{C}_{30}\text{H}_{38}\text{P}_4$	$\text{Si}_5^*\text{Br}_{10}$
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$\text{Si}_2^*\text{C}_{40}\text{H}_{80}\text{P}_2\text{Pt}_2$	$\text{Si}_5^*\text{C}_{15}\text{H}_{46}\text{N}_3\text{P}$
$\text{Si}_2^*\text{C}_{52}\text{H}_{90}\text{P}_2\text{Pt}_2$	$\text{Si}_5^*\text{C}_{60}\text{H}_{50}$
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Si_2^*Cl_6	$\text{Si}_5^*\text{H}_{10}$
$\text{Si}_2^*\text{Cl}_6\text{O}$	$\text{Si}_5^*\text{H}_{12}$
Si_2^*D_6	$\text{Si}_5^*\text{H}_{14}\text{N}_2$
$\text{Si}_2^*\text{F}_5\text{H}$	$\text{Si}_6^*\text{C}_{12}\text{H}_{36}$
$\text{Si}_2^*\text{GeH}_8$	$\text{Si}_6^*\text{C}_{12}\text{H}_{36}\text{Li}_2$
$\text{Si}_2^*\text{Ge}_2\text{H}_{10}$	$\text{Si}_6^*\text{C}_{12}\text{H}_{37}\text{Cl}$
Si_2^*H_6	$\text{Si}_6^*\text{C}_{12}\text{H}_{38}$
$\text{Si}_2^*\text{H}_6\text{LiP}$	$\text{Si}_6^*\text{H}_6\text{O}_3$
$\text{Si}_2^*\text{H}_6\text{O}$	$\text{Si}_6^*\text{H}_{14}$
$\text{Si}_2^*\text{H}_7\text{P}$	$\text{Si}_6\text{Th}^*\text{C}_{18}\text{H}_{54}\text{ClN}_3$
Si_2^*Li_6	$\text{Si}_6\text{Th}^*\text{C}_{18}\text{H}_{55}\text{N}_3$
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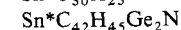
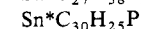
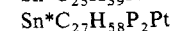
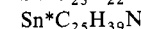
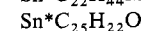
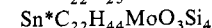
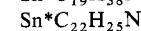
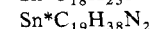
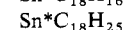
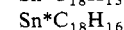
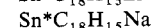
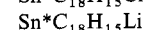
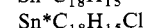
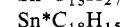
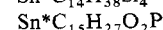
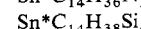
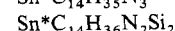
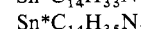
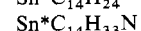
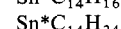
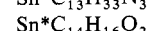
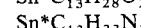
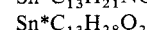
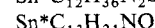
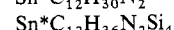
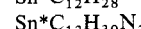
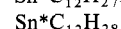
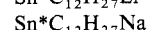
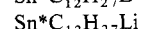
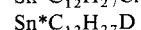
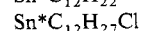
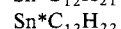
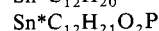
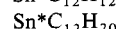
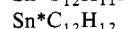
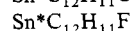
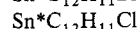
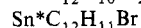
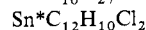
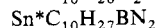
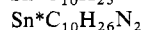
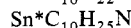
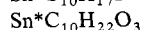
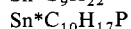
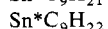
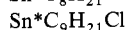
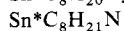
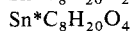
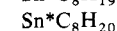
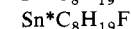
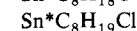
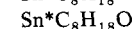
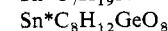
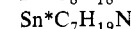
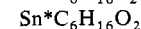
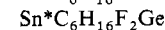
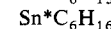
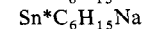
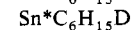
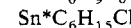
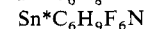
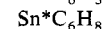
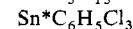
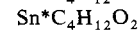
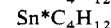
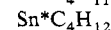
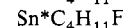
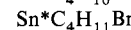
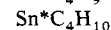
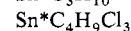
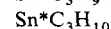
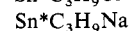
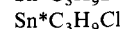
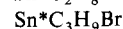
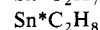
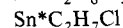
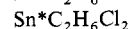
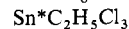
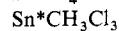
Sm

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**Sn**

Reaction with hydrogen: 1.6.2.4

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Sn*D ₄	Th ₄ *H ₁₅
Sn*GeH ₆	Ti*Be ₂
Sn*H ₂	Ti*C ₄ H ₁₀ Cl ₂
Sn*H ₄	Ti*C ₄ H ₁₀ N ₂ O ₂
Sn*Mg ₂	Ti*C ₄ H ₁₀ O ₂
Sn*O ₈ S ₂	Ti*C ₁₀ H ₁₀ ClMgN ₂
Sn ₂ *C ₆ H ₁₈ Hg	Ti*C ₁₂ H ₁₀ O ₂
Sn ₂ *C ₈ H ₁₈ Cl ₂	Ti*C ₁₂ H ₁₆
Sn ₂ *C ₁₀ H ₂₆	Ti*C ₁₃ H ₂₄ Cl ₂ Mg ₂ NO ₅
Sn ₂ *C ₁₂ H ₃₀	Ti*C ₂₀ H ₃₀ N ₂
Sn ₂ *C ₁₂ H ₃₀ Hg	Ti*C ₂₈ H ₂₅ ClGe
Sn ₂ *C ₁₆ H ₃₈	Ti*Co
Sn ₂ *C ₁₈ H ₂₆	Ti*Cr ₂
Sn ₂ *C ₁₈ H ₂₈	Ti*Fe
Sn ₂ *C ₁₈ H ₄₂ Hg	Ti*FeH ₂
Sn ₂ *C ₂₄ H ₅₄ Hg	Ti*H ₂
Sn ₂ *C ₂₄ H ₅₄ O	Ti*Ni
Sn ₂ *C ₃₆ H ₃₀	Ti*O ₂
Sn ₂ *C ₃₆ H ₃₀ Mg	Ti ₂ *C ₂₀ H ₂₀ ClMgN ₂
Sn ₂ *C ₄₂ H ₄₈ P ₂ Pt	Ti ₂ *C ₂₀ H ₂₂ Cl ₂ N ₂
Sn ₂ *H ₆	Ti ₂ *C ₂₀ H ₂₃ N ₂
Sn ₂ O ₄ *C ₁₈ H ₄₀ N ₂	Ti ₄ *Fe ₂ O _x
Sn ₃ *C ₉ H ₂₇ Sb	Tl*BH ₄
Sn ₆ *C ₇₂ H ₆₂	Tl*B ₂ ClH ₈
Sr	Tl*C ₂ H ₅ O
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Sr*Br ₂	Tl*Cl ₃
Sr*H ₂	Tl*Ga ₃ H ₁₂
Sr*H ₄ N ₂	Tl*H
Sr ₃ *N ₂	Tl*H ₄ Li
Ta*C ₆ H ₂₁ P ₂	Tm*Fe ₂
Ta*C ₁₀ H ₁₃	Tm*H ₂
Ta*C ₁₁ H ₁₁ O	U*C ₁₆ H ₄₀ N ₄
Ta*C ₁₂ H ₁₇	U*C ₁₈ H ₃₀ N ₂
Ta*C ₁₂ H ₃₂ Cl ₂ P ₄	U*H ₃
Ta*C ₁₅ H ₁₈	V*C ₅ HNa ₂ O ₅
Ta*Cl ₅	V*C ₅ Na ₃ O ₅
Ta*H	V*C ₆ HO ₆
Ta ₂ *C ₁₂ H ₃₈ Cl ₆ P ₄	V*C ₉ H ₅ O ₄
Ta ₂ *C ₃₆ H ₉₆ Al ₂ O ₈ P ₈	V*C ₁₃ H ₂₄ Cl ₂ Mg ₂ NO ₅
Ta ₆ *H ₂ S	V*C ₂₃ H ₁₆ O ₅ P
Tb*Co ₂	V*C ₂₆ H ₂₀ O ₃
Tb*H ₂	V*C ₄₃ H ₃₉ BNO ₂ P ₂
Tc*H	V*C ₄₄ H ₃₆ NO ₃
Th*CH ₂	V*Cl ₂
Th*C ₂	V*H
Th*C ₁₈ H ₅₄ ClN ₃ Si ₆	V*H ₂ O ₂
Th*C ₁₈ H ₅₅ N ₃ Si ₆	V ₂ *C
Th*Co ₅	V ₂ *Hf
Th*H ₂	V ₃ Zr ₃ *O
Th*I ₂	W*C ₅ H ₅ ClN ₂ O ₂
Th ₃ *CH ₄	W*C ₅ H ₆ N ₂ O ₂

W*C₅H₇
 W*C₅H₈Cl
 W*C₆O₆
 W*C₇HK₄N₇
 W*C₇K₅N₇
 W*C₈H₆O₃
 W*C₉H₂Cl₄P₃
 W*C₉H₃₃P₃
 W*C₁₀H₅F₃O₅
 W*C₁₀H₁₂
 W*C₁₀H₁₅O₂P
 W*C₁₁H₁₀O
 W*C₁₁H₁₁F₇N₂P
 W*C₁₁H₁₂
 W*C₁₁H₁₂F₆N₂P
 W*C₁₁H₁₃I
 W*C₁₁H₁₄
 W*C₁₂H₁₄
 W*C₁₂H₁₅F₆N₂P
 W*C₁₆H₂₂Cl₄P₂
 W*C₁₈H₁₆
 W*C₁₈H₁₈O₂
 W*C₂₄H₃₃Cl₄P₃
 W*C₂₄H₃₅Br₂N₂P₃
 W*C₂₄H₃₆Br₂ClN₂P₃
 W*C₂₄H₃₉P₃
 W*C₂₇H₃₉Br₂N₂P₃
 W*C₂₈H₃₀Cl₄P₂
 W*C₃₂H₄₄N₄P₄
 W*C₅₂H₄₈N₄P₂
 W*C₅₂H₄₈N₄P₄
 W*C₅₂H₅₀Br₂N₂P₄
 W*C₅₂H₅₁BrN₂P₄
 W*C₅₂H₅₂N₄P₄
 W*C₅₂H₅₆P₄
 W*C₅₂H₅₇F₆P₅
 W*C₅₃H₅₂BrClN₂P₄
 W*C₇₆H₆₄P₄
 W*O₃
 WZr*C₃₁H₄₂O
 W₂*C₁₂H₃₆N₆
 W₂*C₁₆H₁₀O₆
 W₂*C₁₆H₁₁F₆O₆P
 Y*Co₂
 Y*Co₅
 Y*Fe₂
 Y*H₂
 Y*Mg₂
 Y*Mn₂
 Y*Ni₅
 Yb

Reaction with 1-hexyne: 1.10.5.3

Yb*C₁₀H₁₂N
 Yb*C₁₅H₁₈N
 Yb*H₂
 Yb*Ni₅

Zn

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Zn*AlH₃I₂
 Zn*B₂H₈
 Zn*B₃H₁₂Na
 Zn*B₄H₁₆Li₂
 Zn*Br₂
 Zn*CH₃I
 Zn*CH₇B
 Zn*C₂
 Zn*C₂H₆
 Zn*C₂H₇K
 Zn*C₂H₁₀AlLi
 Zn*C₄H₁₀
 Zn*C₈H₁₈
 Zn*C₈H₃₄B₁₂O₂
 Zn*C₁₂F₁₀
 Zn*C₁₂H₁₁Na
 Zn*Cl₂
 Zn*Cr₂O₃-
 Zn*H₂
 Zn*H₂
 Zn*H₂
 Zn*H₃Li
 Zn*H₃Na
 Zn*H₄K₂
 Zn*H₄Li₂
 Zn*H₄Mg

$\text{Zn}^*\text{H}_4\text{N}_2$	$\text{Zr}^*\text{C}_{10}\text{H}_{18}\text{B}_2$
$\text{Zn}^*\text{H}_5\text{Li}_3$	$\text{Zr}^*\text{C}_{11}\text{H}_{11}\text{ClO}$
Zn^*O	$\text{Zr}^*\text{C}_{11}\text{H}_{13}\text{Cl}$
$\text{Zn}_2^*\text{BrH}_3$	$\text{Zr}^*\text{C}_{11}\text{H}_{14}\text{O}$
$\text{Zn}_2^*\text{C}_2\text{H}_9\text{Na}$	$\text{Zr}^*\text{C}_{12}\text{H}_{10}\text{O}_2$
$\text{Zn}_2^*\text{C}_4\text{H}_{13}\text{K}$	$\text{Zr}^*\text{C}_{17}\text{H}_{24}$
$\text{Zn}_2^*\text{C}_4\text{H}_{16}\text{AlLi}$	$\text{Zr}^*\text{C}_{20}\text{H}_{32}$
$\text{Zn}_2^*\text{C}_{10}\text{H}_{28}\text{N}_4$	$\text{Zr}^*\text{C}_{21}\text{H}_{32}\text{O}$
$\text{Zn}_2^*\text{C}_{24}\text{H}_2\text{F}_{20}\text{Na}_2$	$\text{Zr}^*\text{C}_{21}\text{H}_{34}\text{O}$
$\text{Zn}_2^*\text{H}_5\text{K}$	$\text{Zr}^*\text{C}_{22}\text{H}_{30}\text{O}_2$
Zn_3^*As_2	$\text{Zr}^*\text{C}_{31}\text{H}_{42}\text{OW}$
$\text{Zn}_3^*\text{B}_8\text{H}_{32}\text{K}_2$	Zr^*Cl
Zn_3^*P_2	Zr^*Co
Zr^*Br	Zr^*Cr_2
$\text{Zr}^*\text{C}_5\text{H}_6\text{Cl}$	Zr^*H_2
$\text{Zr}^*\text{C}_5\text{H}_{10}\text{B}$	Zr^*Mn_2
$\text{Zr}^*\text{C}_5\text{H}_{13}\text{B}_2$	Zr^*Ni
$\text{Zr}^*\text{C}_8\text{H}_{10}$	$\text{ZrO}_4^*\text{C}_{16}\text{H}_{36}$
$\text{Zr}^*\text{C}_{10}\text{H}_{10}\text{Cl}_2$	$\text{Zr}_2^*\text{C}_{40}\text{H}_{60}\text{N}_6$
$\text{Zr}^*\text{C}_{10}\text{H}_{11}\text{Cl}$	Zr_2^*OPd
$\text{Zr}^*\text{C}_{10}\text{H}_{12}$	Zr_3^*OV_3

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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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